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Final Report

DEVELOPMENT OF INSTRUMENTATION FOR AIRBORNE COLLECTION OF ATMOSPHERIC ORGANIC CHEMICALS

Prepared for:

AMES RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
MOFFETT FIELD, CALIFORNIA 94035

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I INTRODUCTION

This study is the initial phase of a three-phase program designed by National Aeronautics and Space Administration to evaluate and, if results are promising, to exploit airborne organic detection as a tool for determining and classifying planetary biological activity. The program is based on the hypothesis that measurements of the concentration of airborne emanations above regional flora may establish relationships that would permit characterization of flora by airborne sensing instrumentation; the establishment of such relationships would support the concept that planetary atmospheric probes could yield significant information on planetary flora and thus help to characterize any similarities to terrestrial flora.

The presence of organic components in unpolluted atmospheres has long been suspected, but not until 1948, with the use of infrared solar spectra,* was the most concentrated organic constituent, methane, identified. Methane is generally present in the ambient atmosphere at a concentration of about 1.5 ppm. The primary source of methane is bacterial decomposition in swamps, marshes, and other water bodies. In other areas, seepages of natural gas may provide a significant source of atmospheric methane. Lesser concentrations of other low molecular weight saturated hydrocarbons, such as ethane, propane, butane, etc., are also present as minor components in natural gas and could reach the atmosphere in trace concentrations as seepage. Presence in the unpolluted atmosphere of intermediate molecular weight organics such as acetone, methanol, etc., could result from combustion of flora by naturally occurring forest fires or from fermentation processes. The flora of the biosphere is another major contributor of heavier organics of the terpene class. Went estimates that 10^9 tons of terpene-type organics are released to the worldwide atmosphere annually.** The terpene emanations, particularly α- and β-pinene, from conifer forests are well known and are responsible for the "piney" smell found in these areas.

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*Migeotte, M. V., Phys. Rev. 75, 1108 (1949).

**Went, F. W., Tellus, 18(2-3), 549-556 (1966).

As methods of analysis and means of concentration have become more sophisticated, greater numbers of organic atmospheric constituents have been found to be present at extremely low concentrations. The method of approach used in the present study to accomplish the collection of emanations of flora consisted of two phases: (1) a laboratory program to develop appropriate methods of collection and concentration of atmospheric organics, and (2) a field program to test these methods with "real" samples.

II SUMMARY AND CONCLUSIONS

This initial phase has succeeded in developing and field testing techniques for airborne detection of trace organic concentrations. A flight airborne sampling system has been designed. Future phases planned by NASA call for the construction of the flight sampler and its use in high altitude aircraft sampling flights over known types of terrain. If these flights produce useful results, the airborne sampler can be linked to an inflight real-time organic analysis system. A future phase could be the development of a trace organic atmospheric analyzer for planetary probe applications.

A basic part of the design of the sampling system is a concentration procedure that makes use of the ability of gas chromatographic column packing material to selectively retain or trap organics while permitting the permanent gases of the terrain atmosphere to pass through the concentration trap. Sufficient material can be isolated and retained in the system to permit subsequent analysis. The organics of interest for this research program range from methane and other C_1 materials through the C_{10} terpene class of compounds. This broad range of organics requires that the collection system be divided into two channels which then provide efficient collection and concentration for C_1 to C_4 organics on one channel and for C_5 to C_{10} organics on the second channel.

The status of the research can be summarized as follows:

A. Laboratory Program

1. Collection Trap Design

The laboratory work consisted of designing appropriate collection traps for each stage of the C_1 to C_4 and the C_5 to C_{10} concentration procedures. It was necessary to use two successive stages, each with thousandfold concentration, to achieve the 10^6-fold concentration necessary to provide the collection of useful amounts of sample. Cryogenic traps containing gas chromatographic column packing were used for the concentration steps. Liquid argon was used as the cryogen. The C_1 to C_4

organics can be collected and concentrated with a two-stage procedure using a silica gel trap followed by a Porapak Q trap. The C_5 to C_{10} organics can be concentrated with a two-stage procedure using Carbowax 20M followed by an unpacked capillary. Trap design studies included the selection and evaluation of packing material for the several concentration traps. It was necessary to determine the compatibility of the organics of interest with the packing substrate and the efficiency of collection of the concentration stages. Trap efficiency was measured at a variety of known organic concentrations in the laboratory.

2. Dynamic Dilution System

A dynamic dilution system was fabricated for use as a synthetic sample source to permit measurements of the collection efficiencies of the cryogenic concentration procedure at various concentrations similar to those anticipated in the atmosphere. The dynamic dilution apparatus can generate organics at concentrations as low as 1 ppb.

3. Collection Efficiency Measurement

The collection efficiencies of the first-stage collection traps were measured for methane, butane, isoprene, benzene, cyclohexane, and β-pinene at concentrations as low as 1 ppb where possible. Collection efficiencies of the second-stage collection traps were made for the above compounds at higher concentrations which were realistic for the sampler system. Overall efficiencies were also measured for the entire two-stage concentration procedure of collection, transfer, and collection. System efficiencies generally exceeded 85%.

4. Desiccant Evaluation

It is necessary to remove water from atmospheric samples before concentration of the C_5 to C_{10} organic concentration without removing the trace organics.

A number of desiccants were evaluated on the basis of transmission of terpenes without loss or decomposition. Potassium carbonate and calcium chloride were found to be suitable for this application. Potassium carbonate was chosen for use as a desiccant in the airborne collection

system. In addition, methods were developed and tested to remove particulate material from the incoming air sample before the cryogenic traps.

B. Field Program

1. Single-Channel Prototype Organic Sample Collector

The field program used the prototype sample collector to test the methods and techniques developed during the laboratory program on "real" samples collected at ground level in the Coast Range mountains and during one 4-hour airplane test flight over remote areas of northern California. Only the C_5 to C_{10} organics were collected during the field program phase. Collection and measurement of this class of organics provides the most meaningful data on the types and concentration of emanations from flora available by airborne collection. In addition, the C_5 to C_{10} organics are the most difficult to collect and measure, owing to their lack of stability and their extremely low concentrations in the atmosphere; therefore C_5 to C_{10} collection is considered adequate to test the collection principles developed in this research. Tentative identification of organics from vegetation were made in both types of samples.

2. Flight Two-Channel Organic Sample Collector

A prototype organic sample collector suitable for high altitude flight operation was designed on the basis of the experience gained from the laboratory work and from operation of the single-channel sample collector. Although most of the major components have been acquired, time did not permit assembly of the unit.

3. Sample Inlet Probe

The design of the sample inlet probe for the flight unit was based on calculations of ram pressure, boundary layer thickness, and other requirements of the program. The inlet design should present no aerodynamic difficulties.

C. Conclusions

The field tests indicate that the design principles developed during this research program are sound and that collection and measurement of organic emanations can be achieved. Organic constituents of the atmosphere were collected and several compounds tentatively identified by gas chromatographic elution times. Subpart-per-billion quantities of organics were measured by gas chromatography with flame detection on atmospheric samples of two-liter volume. Atmospheric sample volumes of 10 to 20 liters should be adequate for airborne samples taken at higher altitudes.

Absolute identification of specific airborne organics can be achieved with more sophisticated analytical techniques. Thus the ground work for succeeding phases of the overall program whereby flora can be characterized by measurement of airborne emanations has been accomplished. Overflights of regional flora to correlate atmospheric organics with emanations of specific flora will establish the feasibility of characterization of flora by planetary probes.

III LABORATORY PROGRAM

A. Development of Laboratory Equipment

1. Sample Collection and Concentration

The procedure for collecting airborne organics that are present only in trace concentrations consists of passing a known volume of air through a "U" trap packed with gas chromatographic column packing material maintained at low temperature by a cryogen. The permanent gases of the atmosphere pass through the cooled collection tube, while the organic components are quantitatively trapped and concentrated. In the present system two stages of concentration are needed to obtain a sample of sufficient concentration for analysis. The second stage of concentration is obtained by transferring the sample from the first-stage trap and collecting in a much smaller volume second-stage trap. After the organic components of the sample volume have been isolated and concentrated within the first-stage collection trap, the trap is warmed. The organics are thermally released and transferred by nitrogen flow to a cryogenically cooled, small volume, second-stage collection trap. When the transfer has been completed, this final collection trap is sealed, and maintained at cryogenic temperature pending return to the laboratory for analysis. The two types of collection traps are shown in Fig. 1. The present system is capable of increasing sample concentration by a factor of 10^6.

Of the many organic compounds included in the C_1 to C_{10} range of interest in this study, the most trouble was expected in quantitative sampling and analysis of the higher molecular weight compounds such as the terpenes. Thus they were studied in detail. A variety of terpene standards, acquired from chemical supply companies, were subjected to gas chromatography to determine their compatibility with gas chromatographic substrates. Table I lists the terpenes utilized in this analysis. This preliminary investigation served to determine the conditions under which typical terpenes could be collected and analyzed without degradation.

In most gas chromatographic studies, elution time for passage through the column is a significant variable; however, the gas chromatographic elution times of terpenes are difficult to determine, since degradation

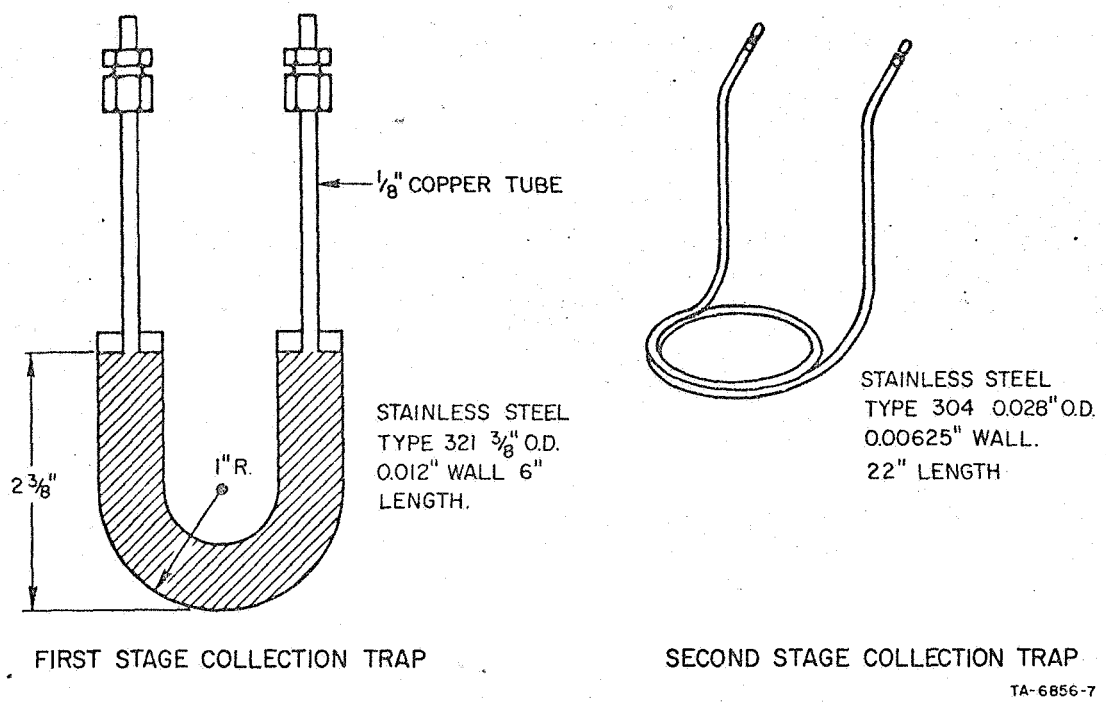

FIG. 1 CRYOGENIC COLLECTION TRAPS

due to polymerization occurs during storage before and after acquisition. In addition some of the terpenes are not readily available as pure compounds and therefore elute from the gas chromatographic columns as multicomponent mixtures.

The relative retention times of the terpene standards using a 20% Carbowax 20M liquid substrate coated on 60/80-mesh Chromosorb W are shown in Table II. The α- and β-ionone terpenes are apparently anomalous in their gas chromatographic behavior, since their rapid elution under our gas chromatographic conditions is unrealistic. The peak consistently observed for α- and β-ionone must be due to an impurity or a degradation product, since the ionones are C_{13} compounds and should be retained longer than the other C_{10} terpenes. Although this could result from thermal degradation within the separation column, it is more likely that with the possible exception of α- and β-ionone this is the result of degradation by time or of impurities present in the standard. Myrcene and camphene were readily available only in technical purity, so that meaningful elution times could not be obtained.

Table I

TERPENES ANALYZED FOR COMPATIBILITY WITH GAS CHROMATOGRAPHY

Terpene	Source in Nature
Iso-borneol	
Iso-bornyl acetate	
DL-Camphene	Natural product and a transformation product from terpene reactions
△-3-Carene	Conifers, oil of turpentine
Citral	Lemon grass, orange
p-Cymene	Essential oils
α-Ionone	Cedar
β-Ionone	Cedar
Isoprene	Terpene precursor
DL-Limonene	Turpentine, citrus trees
Myrcene	Bay tree, hops
α-Phellandrene	Eucalyptus oil, fennel oil
α-Pinene	Conifers, oil of turpentine
β-Pinene	Conifers, oil of turpentine

Table II

ELUTION TIME OF TERPENE STANDARDS RELATIVE TO ACETONE

Terpene	Relative Time
β-Ionone[1]	0.48
α-Ionone[1]	0.50
Isoprene[2]	0.69
Acetone[3]	1.00
α-Pinene	2.0
β-Pinene	3.1
Δ-3-Carene	3.36
p-Cymene	5.65
The following multicomponent mixtures probably result from impurities or degradation during shelf life.	
Iso-bornyl acetate	1.86, 3.3,[4] 5.2
Limonene	0.56, 0.99, 2.55, 4.6
Phellandrene	1.86, 3.38,[4] 4.16, 5.4
Citral	0.51, 0.67
Iso-borneol	15.0,[4] 22.0

[1]The elution time, though consistent, probably is due to an impurity or degradation product

[2]Terpene precursor

[3]Reference organic

[4]Major elution peak

Column:	1/8 inch diameter, 6-foot length, packed with 20% Carbowax 20M on 100- to 200-mesh Chromosorb P
Column temperature:	108°C
Carrier gas:	Helium at 22 cc/min flow
Detector:	Hydrogen flame
Sample size:	0.2 to 0.8 microgram

The organic emanations of flora are complex mixtures of terpenes and other organics whose composition varies with the species of flora. Subsequent degradation of these natural terpenes during their residence time in the atmosphere results in the generation of additional organic components. The net result of this interaction is a broad spectrum of organics present in the atmosphere from the emanations of flora. Thus, the gas chromatographic behavior of pure terpene compounds is only of minor interest. The character of the terpenes does emphasize the difficulty of obtaining even tentative identification of the organics collected from the atmosphere by gas chromatographic retention time alone. Supplemental means of analysis such as a tandem gas chromatograph-mass spectrometer must be employed for organic identification for real samples.

Because different trap packings are needed, separate concentration systems were used for the C_1 to C_4 and the C_5 to C_{10} organics. The first-stage collection trap of the C_1 to C_4 concentration system is packed with 12 g of reagent grade 90/200-mesh silica gel. The C_1 to C_4 second-stage trap is packed with 80/100-mesh Porapak Q. The weight of the Porapak Q was not determined, but was calculated to be 21 µl volume. The first-stage trap for the C_5 to C_{10} organics utilizes 12 g of 20% Carbowas 20M on 60/80-mesh Chromosorb W support. The C_5 to C_{10} organics will be transferred to an unpacked capillary second stage.

B. Evaluation of Prototype Sample Collector Components

1. Dynamic Dilution Apparatus

Cryogenic collection efficiency can only be realistically measured in the laboratory by the entrapment of organics at concentrations similar to that anticipated in the atmosphere, and sample collection must be accomplished at approximately those flow rates to be used during airborne collection. The laboratory system used as a sample source must be capable of generating organic vapors over a wide range of concentrations, as low as 1 ppb. In addition, the synthetic sample source must generate stable organic concentrations over intervals of at least one-half hour.

A synthetic sample source based on multiple dilution techniques and suitable for the measurement of collection efficiency of the airborne sampler was designed and fabricated early in this research program. The three-stage dynamic dilution sample source is shown in Fig. 2. The generation liquid is contained in a vessel of approximately 25-ml volume. A fritted glass disk with a tubulation for the inlet gas is sealed to the base. A wick of asbestos tape extends from the generation liquid 3 to 4 inches into the neck of the vessel. This wick is wet by capillary action over its entire length and thus provides additional area to ensure saturation of the gas by the organic vapor. The asbestos tape also reduces the possibility of carry-over of organic aerosol into the dynamic dilution apparatus. The temperature of the gas at the upper extreme of the wick is measured by a chromel-alumel thermocouple referenced at $0^{o}C$. The thermocouple potential is measured by a Hewlett-Packard Model 425 A microvolt-ammeter. This internal temperature measurement will reflect any cooling effect due to the vaporization of the organic liquid and will represent the actual operating temperature. The temperature of the generator can be measured during operation to an accuracy of $\pm 0.1^{o}C$. The incoming gas stream flows through a 60-inch coiled heat exchanger to assure cooling of the gas to the temperature of the thermostated bath before it enters the generation vessel through the frit. The generator and heat exchanger are submerged in a Dewar flask containing a constant temperature bath. Samples of saturated gas at the output of the generator at various flow rates are chromatographed and compared to the vapor phase of sealed bottles of generation liquid at the same temperature. In this system saturation of the generator gas is complete up through flows of 10 ml/min. Two types of constant temperature baths have been used in the calibration program; ice-water for $0^{o}C$ and dry ice-acetone for $-78^{o}C$.

Four Hastings mass flowmeters purchased to serve as flow indicators in the prototype airborne collection system were installed in the dynamic dilution apparatus. The principle of operation of the Hastings mass flowmeter is based on thermal conductivity measurement and is independent of temperature and pressure. The dynamic dilution system requires gas flow measurements at seven locations for the determination of dilution ratio

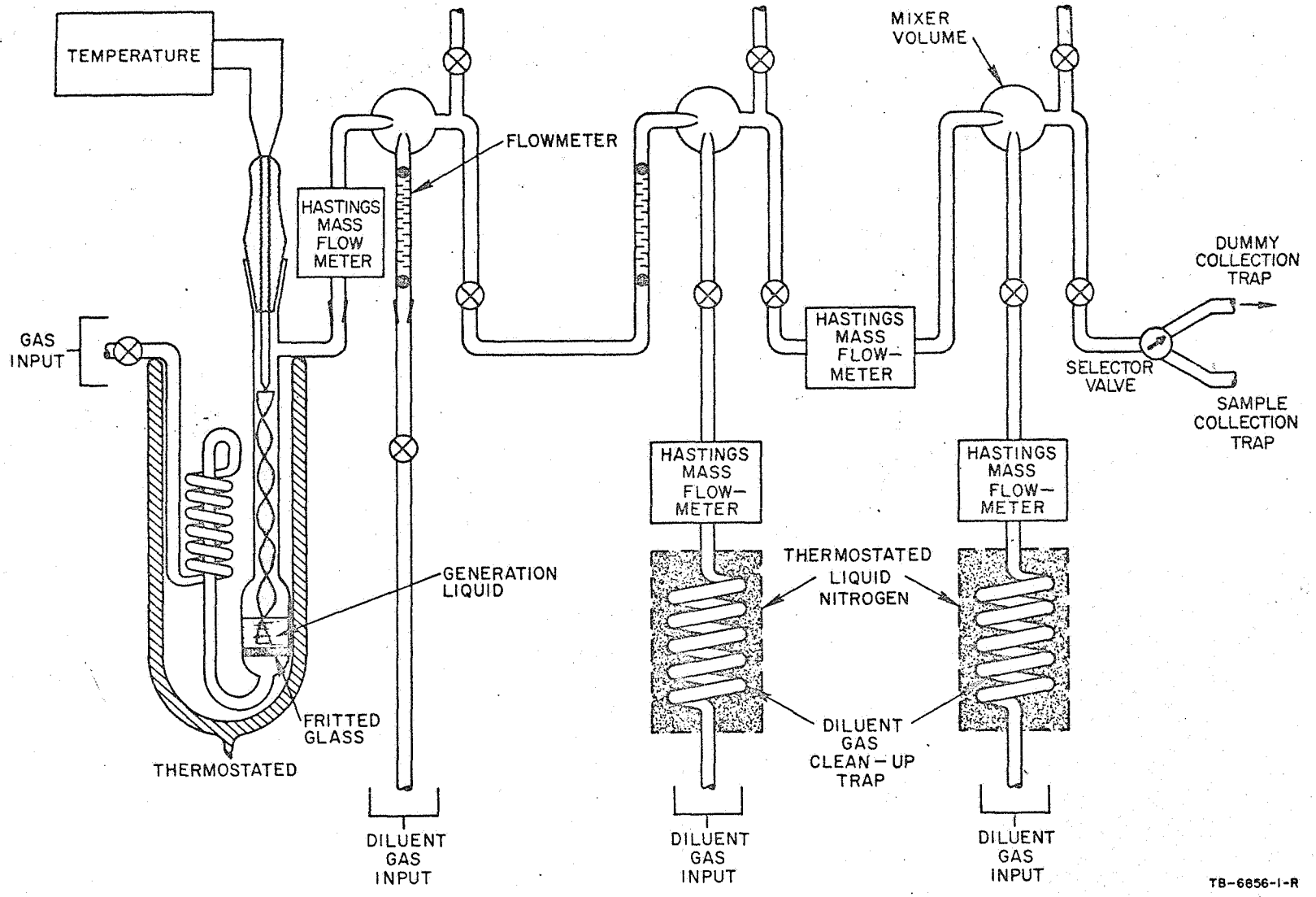

FIG. 2 SCHEMATIC DIAGRAM OF DYNAMIC DILUTION SYSTEM

and total sample collected. It was anticipated that the four Hastings flowmeters could be switched by appropriate valving into the seven gas flow measurement points, but the pressure drop across the low range Hastings flow transducers at normal gas flow rates resulted in a restriction of gas flow in the particular dilution stage being measured. Thus, insertion of the Hastings transducers by valving changed the gas flow rate and hence the dilution ratio of the stage being measured. The Hastings flowmeters were then mounted in fixed locations to measure flows at the more critical points, and other flowmeters were used at the other locations. The Hastings flowmeters are located at the generator output, the second-stage diluent, the third-stage input, and the third-stage diluent. Ball float flowmeters are used at the first stage diluent and at the second stage input. The gas flow passing through the cryogenic collection trap is measured by a displacement type bubble flowmeter.

Ball float flowmeters provide less linear and less reproducible data than Hastings flowmeters. In addition, the ball float flowmeter measurements are subject to error if the internal operating gas pressure, and hence gas density, is different from the operating gas pressure during calibration. The disadvantages of using inexpensive ball float flowmeters can be obviated by operating the dilution apparatus at a constant pressure and adjusting the floats to specific calibrated points. The dynamic dilution apparatus was operated at a constant pressure of 30 psi.

The concentration of organic vapor at the output of the dilution apparatus was calculated as follows:

$$\text{Conc} = \frac{V_P}{P_{std}} \cdot \frac{\text{1st Stage Input}}{\text{1st Stage Diluent}} \cdot \frac{\text{2nd Stage Input}}{\text{2nd Stage Diluent}} \cdot \frac{\text{3rd Stage Input}}{\text{3rd Stage Diluent}}$$

where V_P is the vapor pressure (in millimeters) of test material at operating temperatures, P_{std} is the standard pressure in millimeters, and input and diluent are flow rates in milliliters per minute. Although the concentration can be calculated for any generator temperature and dilution ratio, it is difficult to adjust the parameters with sufficient precision to produce a specific concentration.

The accuracy of organic vapor generation is a function of the measurement accuracy of input flow rates and diluent flow rates of each dilution stage and the temperature stability of the generator. The accuracy of the Hastings mass flowmeters is ±2% of full scale. The accuracy of the ball float flowmeters when used at specific calibrated points is probably within ±2% for the large diluent ball float flowmeters and ±5% for the small input flowmeters. A photograph of the dynamic dilution apparatus is shown in Fig. 3.

Helium is used as the diluent gas in the dynamic dilution apparatus. High purity nitrogen was used initially because it was considered desirable to use a diluent gas similar to air. However, low molecular weight organic contaminants in bottled high purity gases are present at part-per-billion concentrations, and thus it was necessary to add a clean-up step ahead of the dilution system. A 10-inch length of 1/2-inch-diameter copper tube packed with 90/200-mesh reagent grade silica gel cooled by liquid nitrogen was used to trap organic contaminants present in the diluent gas before dilution of the generated organics. However, the dilution system required that the diluent gas have a pressure of 30 psi to achieve the flow rates necessary for high dilution levels, and this applied pressure elevates the boiling point of the diluent gas, resulting in condensation of nitrogen within the liquid nitrogen cooled clean-up stage. This condensation caused erratic fluctuations of diluent gas flow and poor performance of the system. When helium was substituted as a diluent gas, the fluctuations in flow rate were obviated. The clean-up columns were warmed and the trapped organics were released after each day's operation of the dilution system.

In a dynamic dilution system of this type, there is considerable interaction between the flow controls when adjusting the dilution ratios of each stage of dilution. As an example, a change in the dilution flow rate of the second stage will result in changes in the dilution ratio of stage 1 and stage 3. Thus, changes in dilution ratio must be made systematically with only small increments of flow change at any control valve and subsequent adjustment of all other control valves to maintain appropriate direction of gas flow through the entire dilution system. During

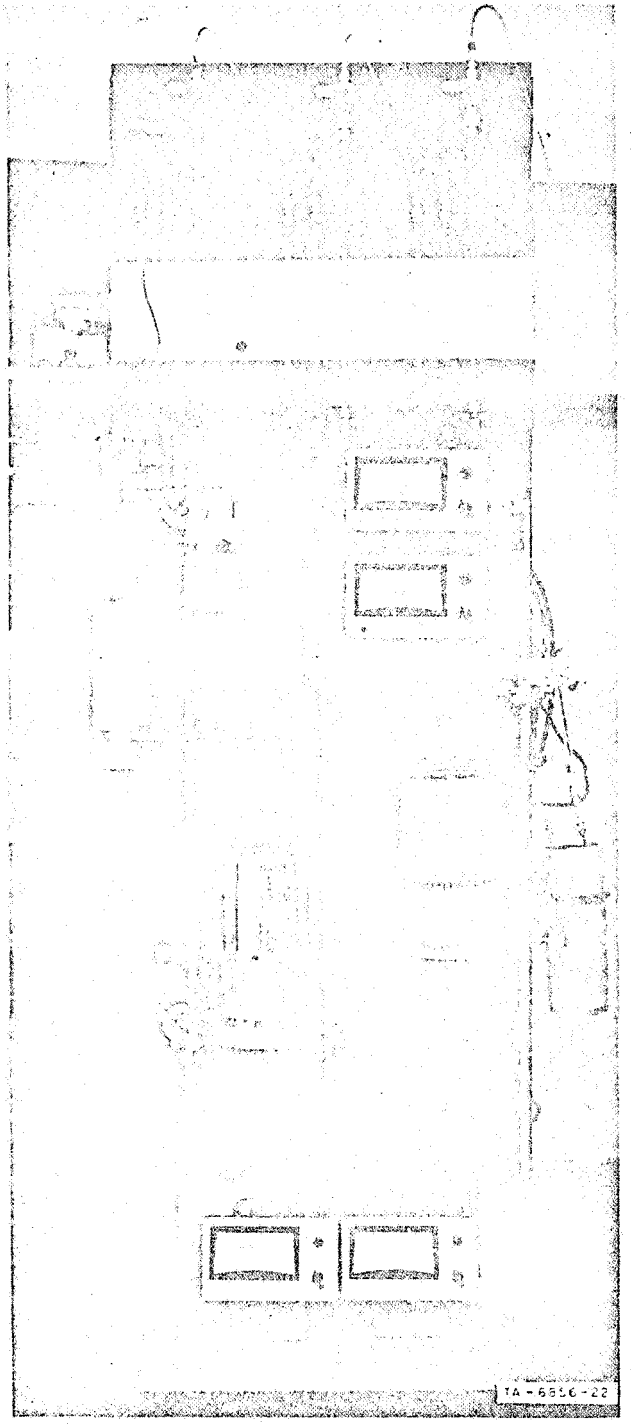

FIG. 3 DYNAMIC DILUTION SYSTEM

generation of low concentrations of organics, this interaction of flow controls is very troublesome and time consuming. Since a dynamic system is subject to continuous absorption-desorption of the organic vapors on the interior surfaces of the dilution system, a change in flow rate of any of the dilution stages results in a change of organic concentration within the system, and a subsequent change in the absorption-desorption equilibrium. The time required for equilibrium and hence concentration stabilization is a function of the degree of concentration change and the dilution stage within which the change occurred. Therefore, particular care must be exercised in operation to avoid sudden bursts or rapid increases in the flow rate of the saturated organic vapor output of the generator. Whenever discrete changes in organic concentration were required or when different organics were generated, the entire dilution system was warmed with an electric heat gun to desorb organics and was operated until a new equilibrium was established.

2. Collection and Measurement with First-Stage Traps

The output of the dilution apparatus flows through a selector valve and permits either a dummy trap or the sample collection trap to be inserted in the sample line. The dummy trap provides a flow conductance similar to that of the collection trap, enabling the dilution ratio to be adjusted and stabilized immediately before sample collection.

The access ports to the first-stage collection trap are fitted with lengths of 22-gauge syringe needles for collection efficiency measurements. The syringe needles are sealed with silicon rubber when not in use to prevent contamination of the trap by laboratory air. Connection to the dilution apparatus was made by injecting the needle tips through a silicon rubber septum sealed to a 1/8-inch Teflon tube connected to the selector valve. After connection, the collection trap was cooled and the sample trap was pressure equilibrated by the addition of helium before being valved into the output of the dilution apparatus. This step was necessary because a partial vacuum was created within the collection trap as a result of cooling from room temperature to cryogenic temperature. Approximately 18 cc of helium was required to bring a trap

to atmospheric pressure. Since the dummy trap has approximately the same flow conductance as the sample collection trap, there was no significant disruption of flow rate and/or dilution ratio when the cryogenic trap was valved to the output of the dilution apparatus. The sample flow rate was measured by a bubble flowmeter at the exit of the collection trap. The time of collection was timed with a stopwatch and the total volume calculated.

The collection efficiency of the cryogenic trap was determined by comparing syringe samples obtained at the output vent of the third dilution stage with the cryogenic collection. The output vent terminated in a long straight length of 1/8-inch stainless steel tubing. The reference sample was collected using a gas-tight syringe to eliminate contamination resulting from syringe barrel blowby. The 6-inch length of the sample syringe needle was inserted into the output vent tube to prevent contamination by laboratory air diffusion into the vent tube during sample collection.

Figure 4 illustrates the general configuration of the sample inlet system used for transferring the cryogenic samples and the reference syringe samples into the gas chromatograph. The reference sample from the bypass was introduced by means of a sample loop connected to the same access ports as were used with the cryogenic collection trap. The syringe samples and the cryogenic samples were collected and preconcentrated in the cryogenic main collection trap before release into the gas chromatograph. This extra concentration step permitted sharp, well-defined gas chromatographic peaks even when appreciable time was required to sweep the sample gas free of the sample loop or cryogenic trap. Two sample loops were used in these calibrations, a 23-cc loop for sample gas of higher organic concentrations and a 100-cc loop for the lowest organic concentrations. The 100-cc loop was the largest practical sample volume that could be used for comparison with the cryogenic sample. Two factors limit the size of the comparison sample volume: (1) the length of time required for the carrier gas of the chromatograph to sweep the loop free of sample gas, and (2) the quantity of background organics present in the carrier gas. Helium was used as a carrier gas in the chromatograph.

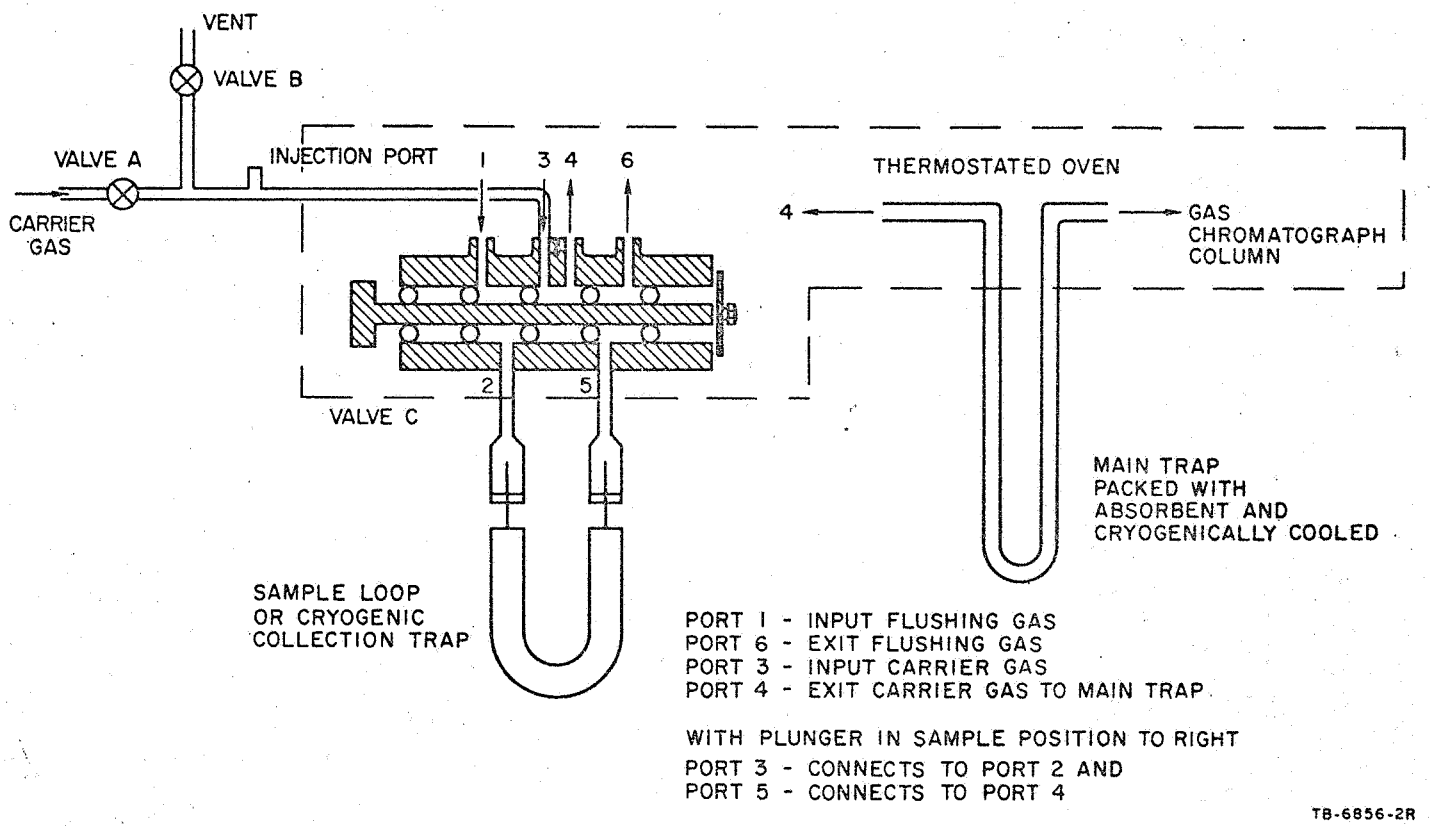

FIG. 4 FLOW DIAGRAM OF SAMPLE INLET SYSTEM

In practice, reference sample gas of at least four times the sample loop volume was obtained from the third-stage vent of the dilution apparatus during cryogenic collection and flushed through the sample loop. As is shown in Fig. 4, the reference gas was introduced through port 1 and exited through port 6 of the sample valve C. When the sample valve plunger was moved to sample position, the sample loop was placed in series with the carrier gas and the reference gas within the sample loop was transferred to the cryogenically cooled main trap. The sample was thermally released from the main trap and analyzed.

Similarly, the cryogenic collection trap was connected to the inlet system by needle-septum connectors. The sample valve plunger was moved to sample position, the sample was thermally released from the collection trap, and was transferred to the main trap.

The collection trap and the main trap were originally warmed with water at 95 to 100°C to elute the sample. Poor chromatographic behavior and losses of the high molecular weight test organics indicated that higher elution temperature was necessary for proper performance. Hot oil maintained at 150°C was used for thermal desorption of the cryogenic traps during the laboratory phase.

As was mentioned previously, silica gel was used as the absorbent for the first stage C_1 to C_4 collection traps. Porapak Q was initially evaluated for this purpose, but considerable difficulty was encountered in quantitatively releasing the organics from Porapak Q by application of heat. The residual organic produced a background that obscured or interfered with subsequent measurements. Apparently the difficulty was a function of the ratio of trap volume to carrier gas flow rate, as no release difficulty was experienced with second-stage traps packed with Porapak Q.

3. Cryogenic Fluids

Liquid argon was used as the cryogenic for the C_1 to C_4 collections. In airborne collection, it is necessary to use argon to minimize the condensation of liquid oxygen within the collection trap. Oxygen has a considerably higher vapor pressure at liquid argon temperatures than at the

liquid nitrogen temperature and can be removed by a nitrogen purge in the airborne sampling unit. The collection efficiency of methane particularly had to be measured at liquid argon temperature to simulate airborne collection efficiencies. It was found to be satisfactory.

The C_5 to C_{10} organics were collected using liquid nitrogen as a cryogen, since these compounds possess extremely low vapor pressures at either liquid argon or liquid nitrogen temperatures. Liquid nitrogen was used as a cryogen whenever feasible, since the cost of liquid argon is ten to twenty times that of liquid nitrogen. Liquid oxygen was used as a coolant in land-based air sampling to prevent condensation within the collection trap. However, liquid oxygen cannot be used in airborne sampling due to the obvious fire hazard.

4. Collection Efficiency of First-Stage Traps

The collection efficiency of the C_1 to C_4 collection trap was determined for methane and n-butane. The collection efficiency of the C_5 to C_{10} collection trap was determined for benzene, cyclohexane, isoprene, and β-pinene. The results of the collection efficiency measurements for specific test organics are shown in Table III.

Although the goal of the calibration was to measure collection efficiencies at concentrations as low as 1 ppb, this could not be achieved with some of the organics without a disproportionate effort and change in basic technique. The accuracy of the collection efficiency measurement is generally poor at very low concentrations of organics, because the comparison syringe samples are barely discernible from the noise. In addition, the diluent gas has background organics in the low part-per-billion range even after silica gel clean-up, and some organics of interest have elution times simular to those of the diluent gas contaminants. Hence not all organics are equally suitable for calibration at low part-per-billion concentrations. Methane offers particular difficulties because it is a contaminant in helium, and it is difficult to remove. In addition, the atmospheric methane concentration of 1 to 2 ppm surrounding the dilution apparatus requires special care in sample handling and technique to avoid contamination. However, after recognizing

Table III

COLLECTION EFFICIENCIES OF FIRST-STAGE TRAPS

Packing	Test Organic	Concentration (ppb)	Collection Efficiency (%)
Carbowax 20M	Benzene	2090	98
		2090	115
		927	118
		866	99
		707	89
		435	96
		87	105
		10	72
		9	79
		3	97
Carbowax 20M	Cyclohexane	325	106
		250	100
		100	113
		48	100
		10	93
		2	100
		0.9	46
Carbowax 20M	Isoprene	427	118
		416	110
		108	100
		108	90
		60	63
		34	77
		7	65
		0.7	51.2
Carbowax 20M	β-Pinene	414	82
		329	80
		228	72
		50	106
		10	102
		2	145
Silica gel	n-Butane	420	103
		408	116
		195	101
		11	91
		3	107
Silica gel	Methane	960	104
		950	85
		367	107
		33	77
		5	106

these limitations on low concentration calibrations, it has been concluded that the present cryogenic traps have good collection efficiencies for the present program.

The low concentrations of isoprene appear to be collected at a lower efficiency than other organics. This can probably be attributed to polymerization of the isoprene within the collection trap.

5. Collection and Transfer Efficiency of Second-Stage Traps

Verification of collection efficiency of the second-stage collection traps is relatively uncomplicated, since organic components of the atmosphere have been concentrated by 10^3 before transfer and collection within the second-stage trap. At these higher concentrations potential sample losses due to surface absorption are insignificant compared to the total volume of trapped organics. The traps used for the second-stage collection have been described previously in the section "Sample Collection and Concentration" and are shown in Fig. 1. The same gas chromatograph inlet system shown in Fig. 4 was used for calibration of the collection efficiency of the second-stage traps. Vapor in equilibrium with liquid organic at a known temperature was used as a sample source for this calibration. Bottles containing the organic liquid were sealed with a rubber septum and thermostated within a constant temperature bath. Microliter quantities of organic vapor were required for collection and transfer efficiency measurements. This type of sample was used with benzene, cyclohexane, isoprene, and β-pinene. For n-butane measurements, the dilution apparatus generator was filled with liquid n-butane and maintained at -78°C to serve as a source of butane at a realistic concentration. A compressed gas cylinder containing 80 ppm of methane in nitrogen was used as the methane source.

The calibration procedure is illustrated by the schematic diagram in Fig. 5. A syringe sample containing a known quantity of organic is injected at point B. The organic is collected in the main trap, thermally released, and the area of the elution peak is determined. A collection efficiency of 100% is assumed based on the collection efficiencies determined previously for the first-stage concentration traps. This main

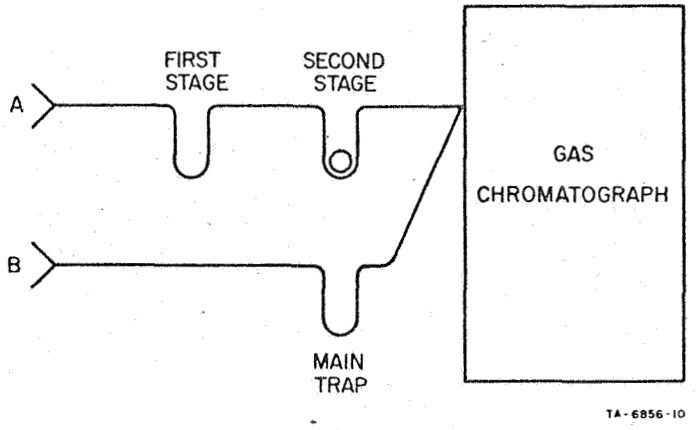

FIG. 5 FLOW DIAGRAM OF TRANSFER EFFICIENCY MEASUREMENT

trap collection is considered as the reference. A similar syringe sample is injected at point A, collected on the first-stage trap, released, and transferred to the second-stage trap. The organic is then released from the second-stage trap and the area of the elution peak is determined. This peak area of the two-step concentration represents the collection efficiency of the entire system proposed for use in the airborne collection unit. The collection efficiencies of the two-step concentration relative to the reference main trap collection are given in Table IV. The data in Table IV are averages of at least three repeats of each collection.

Table IV

COLLECTION AND TRANSFER EFFICIENCIES OF SECOND-STAGE TRAPS

Compound	Main Trap Area Units*	First Stage-Second Stage	
		Area Units*	%
Benzene	230	198	86
Cyclohexane	563	587	104
Isoprene	507	475	93.7
β-Pinene	844	815	96.6
n-Butane	261	254	97.4
Methane	238	218	91.5

* Under elution peak

During the calibration process, the second-stage collection efficiencies were compared with efficiencies of the main trap, as well as transfer efficiencies from first stage to main trap. Since only the two-step concentration procedure will be used for sample collection, the other data are not particularly relevant and therefore were not included. The overall efficiency of the two-stage collection transfer system appears to be satisfactory and does meet the requirements specified for the airborne collection system.

6. Desiccant Evaluation

In the collection of airborne samples, water must be removed from the sample before collection of the C_5 to C_{10} organics to prevent trap clogging by an accumulation of ice. Removal of water is not necessary for C_1 to C_4 organics as the silica gel packing of the first collection stage will remove and hold the collected moisture. The desiccant used for airborne collection of C_5 to C_{10} must retain moisture while passing the organic components of the sample. Since the terpenes and isoprene are the least stable of the C_5 to C_{10} organics and are of particular interest, the stability of these compounds through a packed column of desiccant was used to evaluate the various desiccants considered. β-pinene was used as a typical terpene for the purpose of desiccant evaluation.

The evaluation of desiccant utilized the same sample inlet system as was used for evaluation of collection trap efficiency. This inlet system is shown in Fig. 4. The desiccant oven designed for the airborne system was used for evaluation of desiccants. It consists of a block of aluminum, 1 inch by 3-1/4 inches by 2 inches, heated by a cartridge heater, containing a press-fit stainless steel tube. The stainless steel tube was packed with desiccant and connected to the inlet system at ports 2 and 5 of valve C. The electrical input to the cartridge heater was controlled by a variable voltage transformer and the temperature was monitored by a thermocouple.

After considerable experimentation, two desiccants, potassium carbonate (K_2CO_3) and calcium chloride ($CaCl_2$), were found that pass isoprene

and β-pinene with transmission efficiencies of about 100% at temperatures of 50 to 60°C. Tests were made to determine the difficulty in operation especially flow rate changes, due to the deliquescent nature of both K_2CO_3 and $CaCl_2$. Two identical tubes packed with 4-mesh $CaCl_2$ and 20- to 50-mesh K_2CO_3 were exposed to 55 liters of air saturated with water vapor at room temperature. The entire length of the packed tube containing $CaCl_2$ appeared to be moist after exposure to the 55 liters of air. No change in flow rate was apparent, but water removal was obviously incomplete. A deliquescent appearance of the tube packed with K_2CO_3 was noted at the entrance, and little change in resistance to flow was apparent. The difference in desiccant efficiency of $CaCl_2$ and K_2CO_3 could be due to mesh size, but since the 20- to 50-mesh K_2CO_3 appears to have suitable characteristics for this research program, this facet was not explored further. The K_2CO_3 tube was repacked with a back-up length of indicating Drierite ($CaSO_4$) following the K_2CO_3. The indicating Drierite did undergo a color change with passage of water saturated air, indicating that the K_2CO_3 does not remove water vapor as completely as Drierite. However, sufficient water is removed to make K_2CO_3 suitable for use as a desiccant in the airborne sampling system. Additional experiments verified that terpene transmission efficiencies are excellent with K_2CO_3 at room temperature.

The identification of the suitability of these two desiccants occurred only after many desiccants were evaluated and found to be unsuitable for this application owing to irreversible absorption or decomposition of terpene. The following paragraphs describe the other desiccants studied.

Calcium carbide was evaluated as a desiccant at elevated temperatures, but did not prove to be feasible, as isoprene and terpenes decomposed on contact. Calcium hydride at elevated temperatures was also evaluated as a potential desiccant. However, it was not useful owing to terpene decomposition upon contact. Calcium sulfate (Drierite) was evaluated at temperatures up to about 100°C. Although transmission of isoprene and several terpenes did approach 85% at times, the transmission percentage varied. Conditioning of this desiccant by repeated injections of terpenes improved the transmission efficiency; however, it was not considered to be adequate for this application.

Molecular sieves 4A and 5A irreversibly absorbed the terpenes. Magnesium perchlorate (Dehydrite) irreversibly absorbed terpenes but passed isoprene at about 87% transmission. Silica gel did not pass the β-pinene at temperatures up to 100°C. Anhydrous sodium sulfate (Na_2SO_4) was found to decompose β-pinene at temperatures of 85°C and up. When Na_2SO_4 is maintained at temperatures of 33 to 60°C, transmission efficiencies of 15 to 40% are found for β-pinene.

7. Aerosol Entrapment by Cryogenic Collection Traps and Filters

Another facet of research is concerned with the aerosol trapping efficiency of the cryogenic trap and the efficient removal of particles larger than 1 μ. Measurements were made of the retention of small particles by the C_5 to C_{10} cryogenic traps packed with Carbowax 20M. Airflow rates through the traps were varied from 100 to 400 cc/min. Aerosols of sodium chloride and lithium fluoride were used, varying in size from 0.007 to 0.12 μ diameter (median) with log-normal distributions. The collection efficiency in all cases was 99 to 100%.

A "clean room" was used as an aerosol chamber in which a desired concentration of aerosol particles could be produced. The chamber could be cleared to essentially zero concentration of aerosol particles in a few minutes. The aerosols were generated with a Devilbis Type 44 nebulizer at 6 psi air pressure from aqueous solutions of sodium chloride and lithium fluoride. The initial drop size distribution remained constant; thus upon evaporation the mean particle diameter was proportional to the 1/3 power of the concentration. For the smaller particles (0.015 μ and smaller) lithium fluoride was used to assure complete evaporation of particles. Larger particles of lithium fluoride could not be produced in this manner because the solubility is too low. Previous studies with this technique have not indicated any differences between the sodium chloride and lithium fluoride particles with regard to size and concentration measurements. Size distributions obtained with this technique have been determined by electron microscope measurements and are indicated in Fig. 6 without specific data points being indicated. A GE nuclei counter was used to monitor both the test chamber particle concentration and the post cryogenic trap concentration.

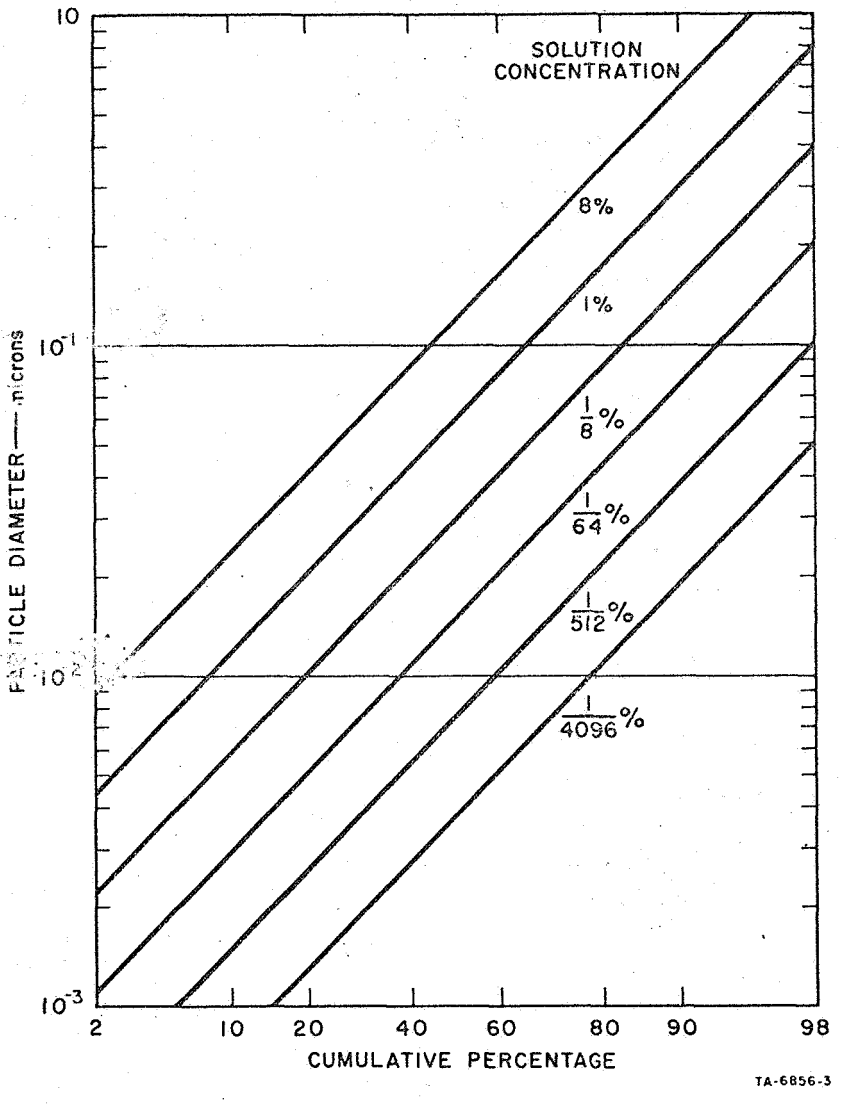

FIG. 6 SIZE DISTRIBUTION OF GENERATED AEROSOL

Operation of the aerosol generator under constant conditions gave reproducible concentrations of aerosol for all solution concentrations. The lower limit of sensitivity of the counter was taken as 200 nuclei/cc. In each case a test aerosol of 2×10^4 particles/cc was produced in the chamber.

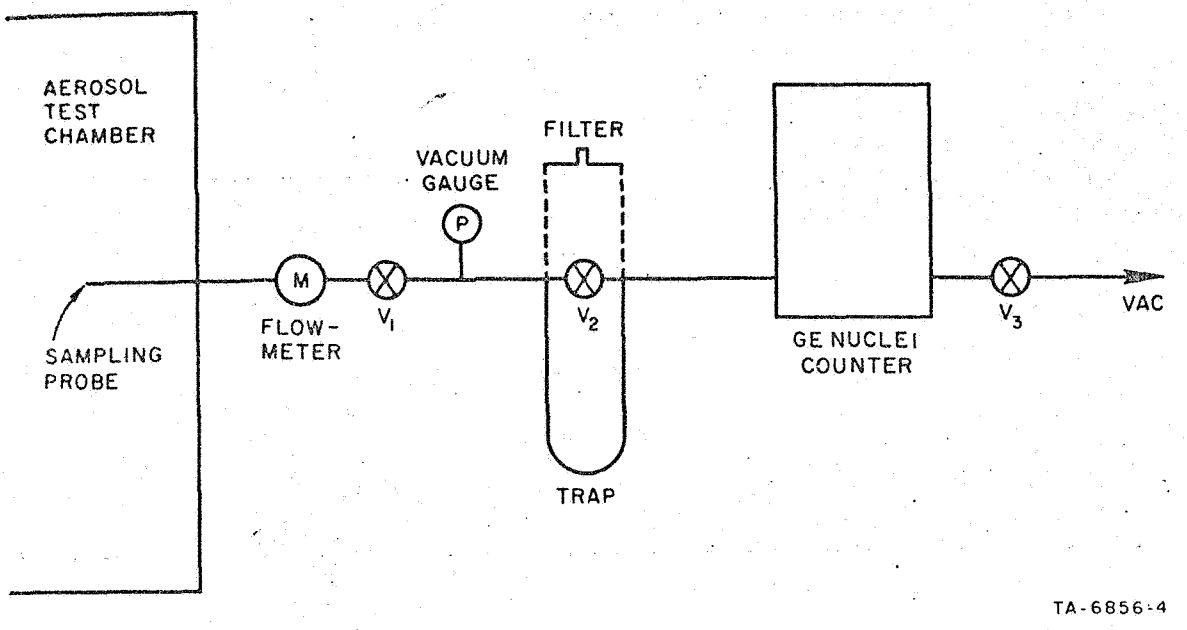

FIG. 7 AEROSOL ENTRAPMENT EVALUATION EQUIPMENT

The sampling and measurement setup is shown in Fig. 7. The aerosol is drawn from the test chamber through a flowmeter, then through the trap being tested, and finally through a GE nuclei counter. When valve V_2 is opened the aerosol bypasses the trap and a measurement of the concentration in the chamber is obtained. By closing valve V_1 it is possible to operate the trap at lower pressure. It was established that the flowmeter, valve V_1, and variation of the vacuum on the GE counter did not affect the aerosols or the performance of the counter to a perceptible degree. Measurements were made with the traps immersed in liquid oxygen.

No detectable concentration of particles penetrated the trap in any test; thus the collection efficiency was always 99 to 100%. Two runs were made for each set of conditions of particle size, flow rate, and pressure (see Table V).

Some measurements were also made with filters by inserting a filter holder in place of the traps. The particle retention of two types of filters is shown in Table VI. The removal of particles larger than 1 μ without the loss of submicron particles does not appear to be feasible with filters.

Table V

PARTICLE RETENTION BY COLLECTION TRAPS

Median Particle Diameter (μ)	Pressure (atm)	Flow Rate (cc/min)	Collection Efficiency (%)
0.12	1	400	95-100
	1	200	
	1	100	
	0.5	100	
0.06	1	400	
	1	200	
	1	100	
	0.5	100	
0.03	1	400	
	1	200	
	1	100	
	0.5	100	
0.015	1	400	
	1	200	
	1	100	
	0.5	100	
0.0075	1	400	
	1	200	
	1	100	
	0.5	100	

Table VI

PARTICLE RETENTION BY FILTERS

Median Particle Diameter (μ)	Pressure (atm)	Flow Rate (cc/min)	Retains (%)	Type of Filter
0.0075	1	300	110	Flowtronics FM47-1.2 μ 47 mm diameter
0.030	1	1000	100	
0.12	1	2000	100	
	1	5000	100	
0.30	1	300	99	Whatman No. 1, 47 mm diameter circular
	1	1000	90	
	1	2000	85	
0.12	1	300	96.7	
	1	1000	87	
	1	2000	80	

There appears to be some uncertainty as to whether complete removal of particles, submicron as well as those larger than 1 micron, is necessary for the collection of airborne organics. Therefore, two approaches for the prototype airborne collection system are available. A sintered silver filter such as Flotronics Membrane FM47-1.2 μ with a pore size of 1.2 μ would remove essentially all particles regardless of size. The sintered silver construction material would permit clean-up and removal of organics by high temperature bake-out before installation in the collection system. The other approach is particulate removal by means of an impactor.

A two-stage impactor has been designed to remove all particles larger than 1 μ diameter, with a sharp cutoff in collection at 1 μ. The two-stage design reduces the possibility of particle re-entrainment and collection in the cryogenic trap. This two-stage impactor, shown in Fig. 8 has not been fabricated or tested; however, the design principles are sound, and operational difficulties are not anticipated.

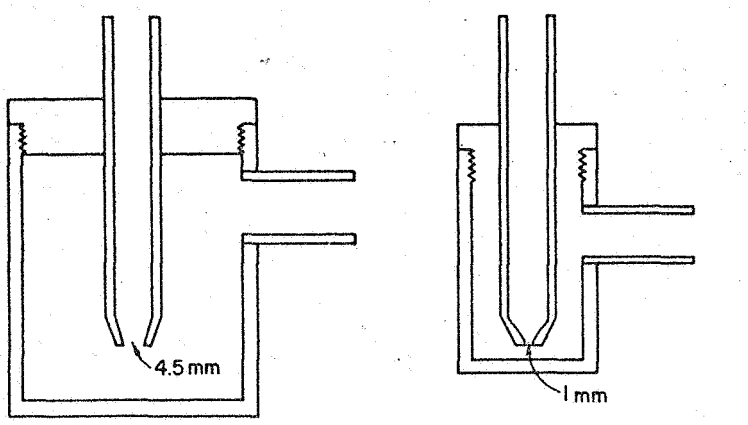

FIG. 8 TWO-STAGE IMPACTOR PARTICLE COLLECTOR

8. Concentration Factor Measurement

The concentration factor is the ratio of sample volume to the internal volume of the body of the final concentration stage. As an example, if all the organics contained in a 10-liter atmospheric sample are concentrated and collected in a collection trap of 10 μl volume, then a concentration factor of 10^6 has been achieved. The concentration system in this research program was designed to concentrate by a factor of approximately 10^6, with each stage of concentration contributing a concentration factor of 10^3. The volumes of three first-stage packed collection traps were measured and found to be 6.5, 6.85, and 7.1 cc. Two methods of volume measurement were used; excellent agreement was obtained. The collection trap, maintained at room temperature, was flushed with 80 ppm methane, and the trap volume of gas was swept into a gas chromatograph where the quantity of methane was determined. The other volume measurement was made by evacuating the trap, then measuring the volume of gas required to equilibrate to atmospheric pressure.

The volume measurement of the second-stage collection trap was extremely difficult to achieve. Therefore, since a known concentration factor is not necessary to the operation or calibration of the airborne sample collection system, the volume of the second-stage trap was calculated rather than measured. The volume of the unpacked capillary second-stage trap is 71 μl. The volume of the packed second-stage trap was not determined but calculated, on the basis of a 50% volume packing factor, to be about 38 μl volume. The design aim for the trap volume is 10 μl. However, capillaries of smaller cross section could easily clog during operation and shorter lengths would not collect organics as efficiently.

Therefore, with the present design of second-stage collection traps, an atmospheric sample volume of 71 liters would be required to achieve a concentration factor of 10^6. However, subpart-per-billion concentrations of organics in the atmosphere are detectable with sample volumes of one to two liters.

C. Single-Channel Prototype Airborne Sample Collector

A single-channel airborne sample collector was designed and fabricated to test the principles and developments evaluated in the laboratory program. Only the C_5 to C_{10} organic collection channel was used for field testing of the airborne sample collection device. The C_5 to C_{10} class of organics represents by far the more difficult group to collect, owing to their low vapor pressure and hence extremely low concentrations in the atmosphere. The C_5 to C_{10} organics are also the most difficult to concentrate, since they are far less stable than the C_1 to C_4 class. In addition, with the limited time available for field sample collection, the collection of C_5 to C_{10} organics would provide the maximum information about the concentration of terpene emanations from flora available from airborne sample collection. The basic design of this collection system is shown in Fig. 9. The inlet to the airborne collection system contains a packed column of potassium carbonate maintained at room temperature, in addition to the desiccant oven section. This additional desiccant stage lengthened the operating life of the desiccant contained in the desiccant oven, thus eliminating repeated assembly and disassembly to replenish desiccant.

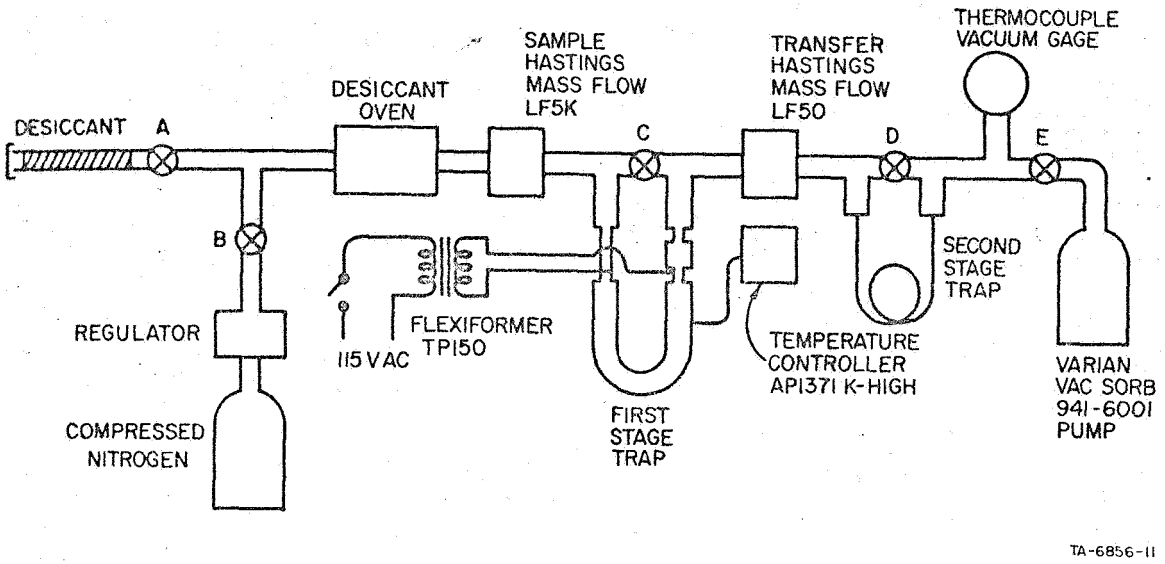

FIG. 9 SCHEMATIC DIAGRAM OF PROTOTYPE AIRBORNE SAMPLE COLLECTOR

In the prototype sampling system the collection procedure and sequence of operation is as follows: the sample inlet is unsealed, valve B is opened, with valve A closed and valves C, D, and E open; this permits the system to be flushed with compressed high purity nitrogen for two to three minutes at a flow rate of 530 ml/min. The first-stage trap is cooled with liquid argon during the flushing process. At the end of the flushing interval, the system is evacuated by closing valve B. Evacuation removes any residual air in the system. After system evacuation, valve C is closed and sampling is initiated by opening valve A. The sample flow rate is measured by the sample Hastings mass flowmeter. The time of the collection is measured by a stopwatch.

After a suitable sampling interval, 5 to 8 minutes, valve C is opened, valve A is closed, and the system is flushed with nitrogen for three minutes by opening valve B. This completes the first-stage collection step. This flushing removes sample air from the system that could interfere with succeeding transfer operations.

The second-stage trap is now cooled cryogenically, and when it is at cryogenic temperature, valves B, C, and D are closed. As soon as the flow indicated by mass flowmeter B has reached a level of 10 to 15 ml/min, valve B is adjusted to maintain and stabilize the system flow at this rate. After flow stabilization, the liquid argon Dewar is removed from the first-collection stage and resistance heating of the first-stage trap is initiated. This heating releases the organics collected in the first collection stage and transfers them to the cooled second stage. The transfer flow rate is 10 to 15 ml/min. The release temperature of about 130°C for the first collection stage is monitored and controlled by an API Model 371K-High Compack II temperature controller. It takes eight minutes to transfer the organic sample to the second-stage trap. After termination of the transfer interval, valve D is opened, valve E is closed, and the system pressure is increased to atmospheric with nitrogen. The second-stage trap is disconnected at the septum connector, sealed with silicone rubber plugs, and rapidly transferred to a large "holding" Dewar of liquid nitrogen, where it is held until analyzed. Another second-stage trap is installed in the airborne collector system. Valves C and D are closed, valves E and B are opened, and the system is again flushed for two to three minutes at 580 ml/min with nitrogen. This procedure ensures that air introduced during septum puncture by the trap and the air contained within the second-stage trap do not contribute to the succeeding sample collection. At this point the sample collection cycle is complete and the collection system is ready for the succeeding sample. The complete cycle requires about 24 minutes; therefore, two samples per hour can be collected.

The rate of sample flow is limited to about 280 ml/min primarily by the flow conductance of the transfer Hastings mass flowmeter, which is continuously in stream with this breadboard sample collector. The flight two-channel collector includes a bypass valve to obviate this flow rate restriction. The flight two-channel collector will have two operationally independent channels allowing concurrent collection and transfer of C_1 to C_4 and C_5 to C_{10} organics. The collection and transfer times could obviously be shortened by higher flow rates, but these tentative collection, transfer, and flushing intervals are acceptable; more experience in collecting real samples may well suggest changes.

The prototype sample collector is approximately 36 inches high, 30 inches wide, and 15 inches deep, and weighs about 50 pounds. The same major components are used in this prototype unit as will be used in the flight instrument. Thus the performance of the major components was evaluated during the field tests as well as overall system performance. A photograph of the single-channel prototype sample collection is shown in Fig. 10.

The Varian Model 941-6001 Vac Sorb pump is a trouble-free vacuum pump that provides vacuum capability without contributing potential organic contamination to the sample. The capacity of the Vac Sorb pump is described by the manufacturer as 100 liters. This capacity is based on the capability of reducing the pressure of a 100-liter volume from atmospheric to 10^{-1} torr in less than five minutes. Although the single pump capacity has proven to be adequate for sampling with the single-channel sampler, two pumps connected in parallel will be used for the flight airborne collection system. Inflight regeneration of the Vac Sorb's molecular sieve packing can be accomplished if extended sampling times or large numbers of samples are to be collected.

The thermal release of the organics from the first-stage collection trap on the sampler unit differed from the procedure used in the laboratory tests, since heating of the trap in the airborne system is accomplished by resistance heating of the stainless steel trap body rather than by a hot oil bath. Some difficulty was encountered during testing and checkout of this new thermal release procedure. It was concluded that uneven heating of the first-stage traps produced local hot spots, and apparently resulted in volatilization and decomposition of the packing substrate. Although these hot spots are not externally discernible, the decomposition of the packing resulted in condensation of the decomposition products in cooler areas of the sample collector system and disturbed the system operation. This contamination required disassembly and cleanup of the sample collector before additional air samples could be collected. The uneven heating is believed to be due to stresses resulting from the short radius "U" tube bending of the stainless steel trap body during fabrication. Heating of the stainless steel tube to a red heat to relieve stress before packing

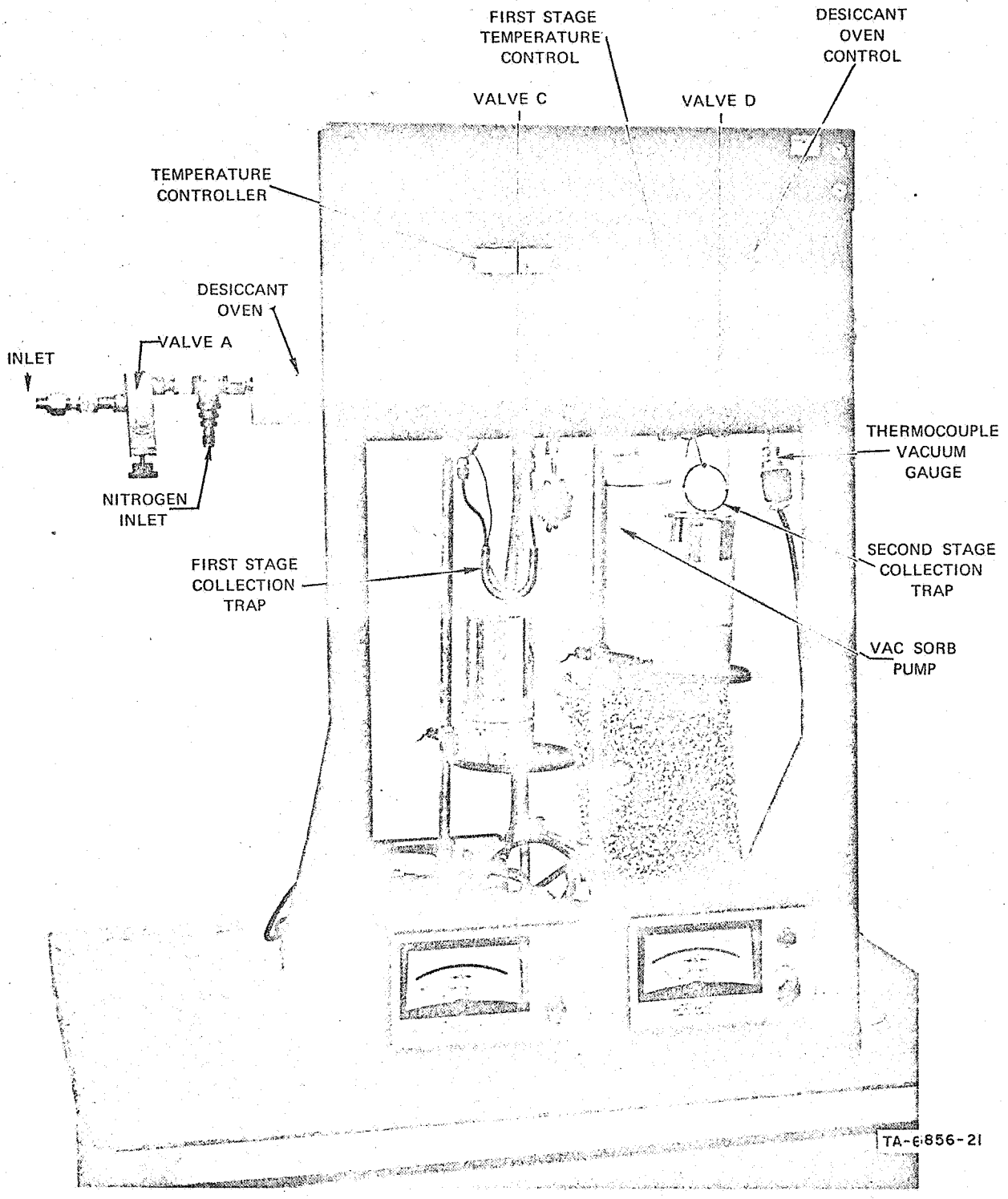

FIG. 10 PROTOTYPE AIRBORNE SAMPLE COLLECTOR

with Carbowax 20M should reduce the degree of uneven heating. This avenue was not pursued, as a reduction in applied voltage with a subsequent longer release time obviated the difficulty. The decomposition appeared to be a function of rate of heating rather than the ultimate temperature attained. The release temperature used for airborne samples was about 130°C, at which no decomposition of the packing material was apparent. An empty Dewar flask was placed over the first-stage trap during thermal release of the organics to eliminate changes in temperature due to breezes.

Another design problem encountered with the single-channel sample collector was the method of assembly. For ease of disassembly and for ease of changes in design, the single-channel unit used Swagelok connectors and tapered pipe thread fittings with Teflon tape as a sealant. However, the Teflon tape contains organics that must be removed by bake-out of the entire system, and our experience now indicates that Teflon tape should be used only where absolutely necessary, i.e., the threaded ports to the Hastings mass flow transducers. The Swagelok fittings are vacuum tight when first assembled, but with repeated assembly and disassembly, they become increasingly difficult to keep leak-free. The flight collector design will incorporate welded or silver-soldered fittings whenever possible. If Hastings mass flow transducers with weld-type connections could be obtained, their use would be highly desirable in the two-channel flight collection system.

Another minor problem was encountered with the single-channel system during transfer of the sample from the first-stage trap to the second-stage trap. Sometimes blockage of the second-stage trap would occur after about five minutes of transfer flow. A sudden drop in transfer flow rate indicated that blockage had occurred. Ice formation was suspected, resulting from inefficient drying. The flow could be re-established by warming the second-stage trap at the point of entrance into the cryogenic fluid. Warming was conveniently accomplished by momentarily gripping the capillary trap with a pair of pliers. In an attempt to determine the cause of the blockage, Dehydrite was substituted for K_2CO_3 as a desiccant. Although Dehydrite is unsuitable in the operating system because of organic decomposition, it is an excellent desiccant and provides very

complete removal of water. However, occasional blockage still occurred even with Dehydrite, thus eliminating the possibility of ice formation due to incomplete water removal by the K_2CO_3. Solid CO_2 was also considered as a possible interfering material and ascarite followed by K_2CO_3 was used to remove both CO_2 and water from the sample. However, occasional blockage still occurred. The cause of this flow problem has not been resolved; however, since the blockage can be alleviated easily, no further experiments were performed to discover the cause.

IV FIELD PROGRAM

A. Results of Ground-Based and Airborne Sample Collection

Two field trips were made to test the collection system for ground-based operation. The sampling site was about one mile west of Skyline Boulevard on Bear Gulch Road in the Coast Range mountains near Stanford Research Institute. The area is heavily wooded with conifers, primarily redwood trees, and is sparsely populated. The initial sampling occurred on July 23, 1968, when three samples were collected. The power control setting for electrical heating of the first-stage had been disturbed during transit, and this was not discovered before operation of the unit. Some thermal decomposition of the column packing resulted, with subsequent contamination of the system. The results of this sample collection were therefore subject to question.

A second field trip to the same sampling site was made on July 26, 1968. A gas chromatogram of the initial sample, 1900 cc taken under calm wind conditions, is shown in Fig. 11. The high concentration of low molecular weight components can probably be attributed to an accumulation of exhaust fumes from logging trucks or from our own vehicle; however, the presence of late eluting compounds could be due to an accumulation of emanations from the forest during the period of calm. Before samples 2 and 3 were taken, a breeze began from the northwest, providing sample air with less likelihood of contamination. Samples 2 and 3 are of 1120 cc and represent samples taken under similar northwest wind conditions (Fig. 12) 30 minutes apart. Reasonable duplication is apparent. As was mentioned previously, identification, or even tentative identification, of elution peaks is extremely difficult without supplementary analytical means. An indication of relative elution times of terpene standards with acetone as a reference compound is shown below these gas chromatograms. The separation column used was 6 feet in length packed with 20% Carbowax 20M or Chromosorb W. A column temperature of 108°C was used.

Unfortunately, land-based samples in generally accessible areas are difficult to interpret because potential sources of contamination such as vehicles are always nearby and their contribution to airborne organics is quite unpredictable.

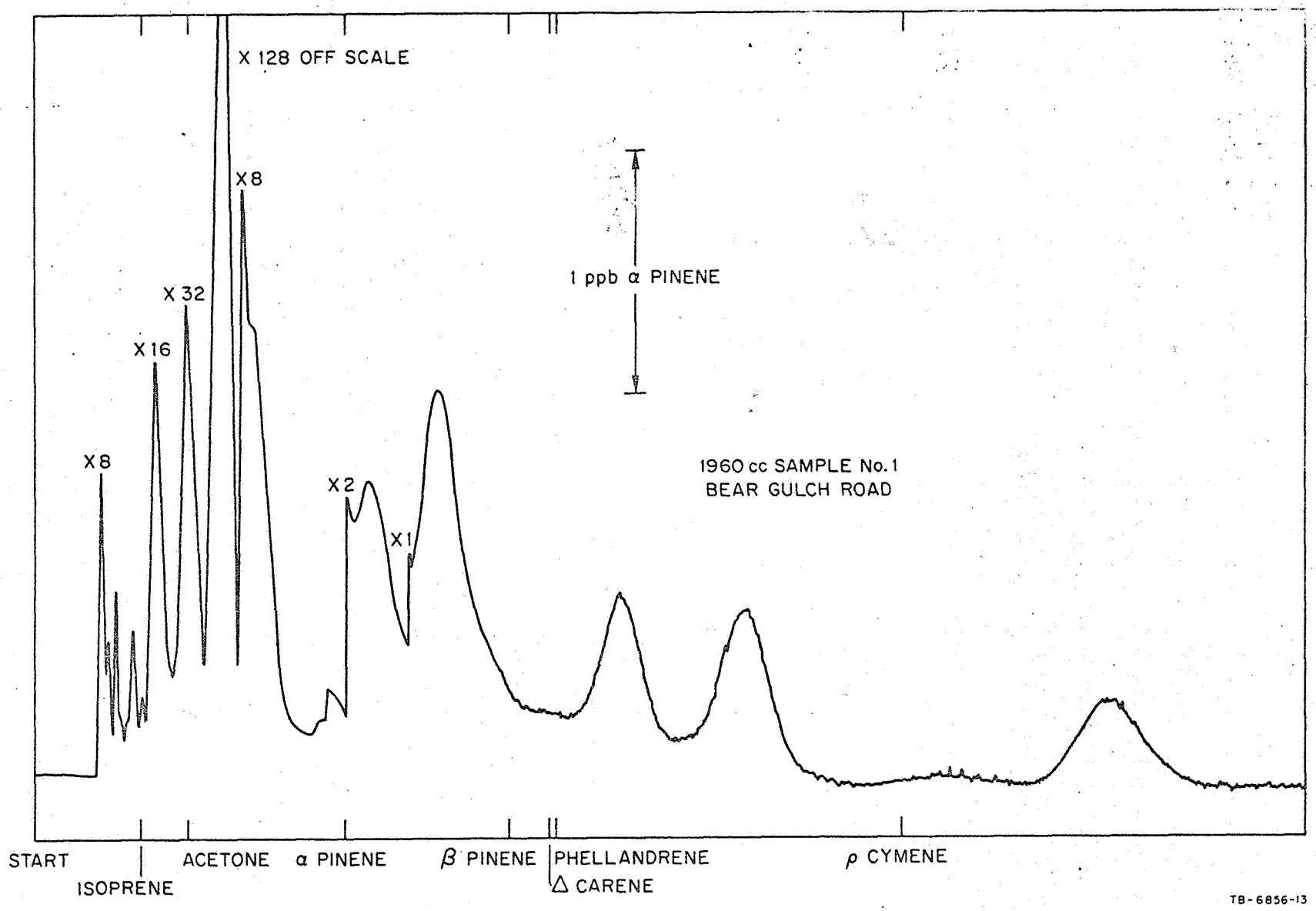

FIG. 11 GAS CHROMATOGRAM SAMPLE NO. 1, BEAR GULCH ROAD

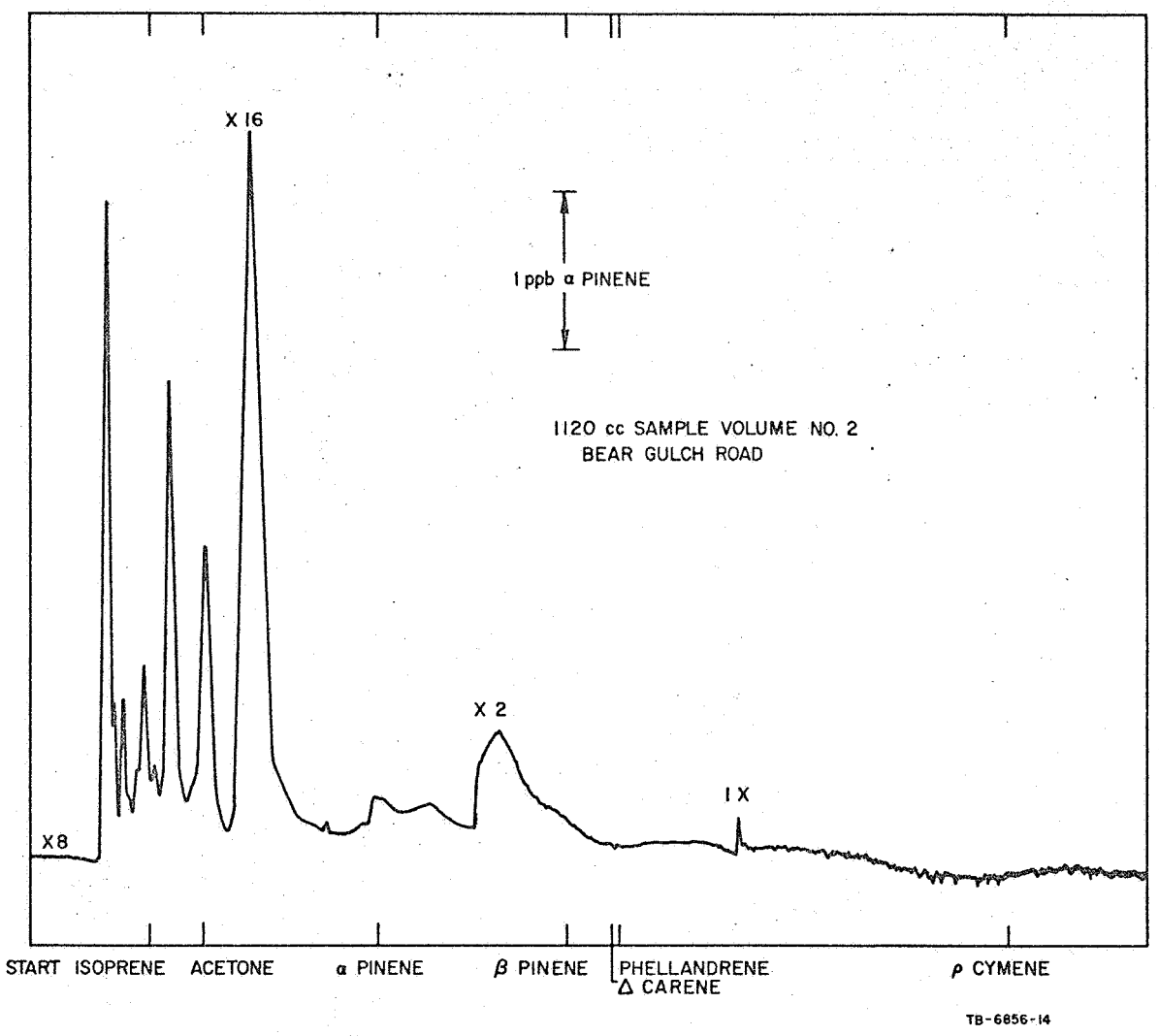

FIG. 12(a) GAS CHROMATOGRAM SAMPLE No. 2, BEAR GULCH ROAD

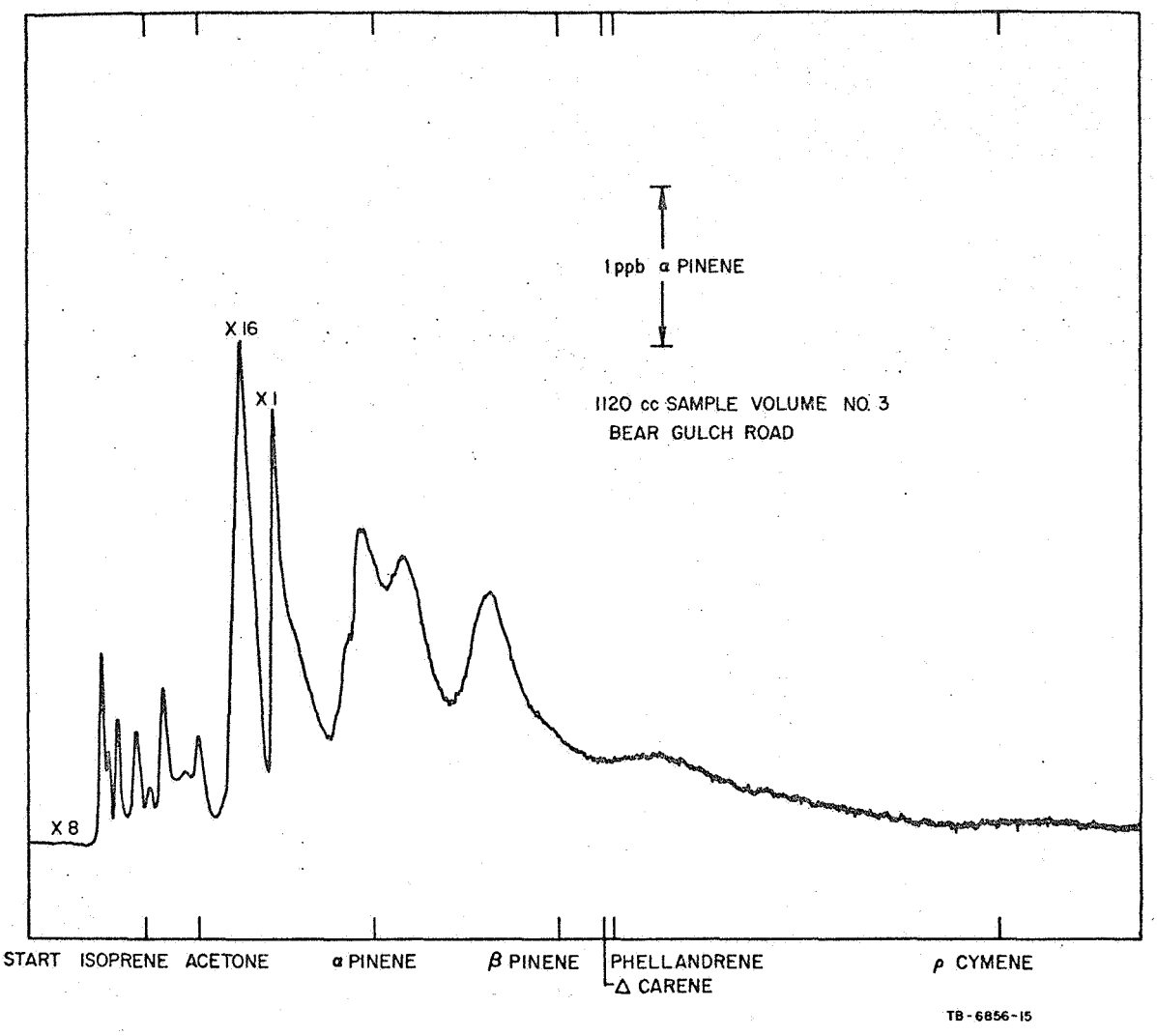

FIG. 12(b) GAS CHROMATOGRAM SAMPLE NO. 3, BEAR GULCH ROAD

In an attempt to get a better picture of vegetation emanations, airborne samples were taken on August 7, 1968, over the Coast Range of northern California. The aircraft used was a Twin Beechcraft with a sample probe of new 1/2-inch copper refrigeration tubing. The sample probe inlet was on the nose of the aircraft 2-1/2 feet forward of the propeller arcs. This location ensured that air exposed to the engine and thrown outward by centrifugal force from the propeller would not contaminate the sample. Although previous experience has shown that sealed refrigeration tubing is remarkably free of organics, the tube was flushed and equilibrated with incoming air for one hour during transit to the sample location. The prototype organic sample collector was sealed during the transit interval.

The sampling area chosen for airborne testing is a sparsely populated, mountainous terrain covered by a dense conifer forest. There are several sawmills in the area; however, the smoke plumes from the sawmill waste burning are easily visible from the air and can be avoided. Most of the air samples were obtained within 1/2 mile to 5 miles of the coasts and from 10 miles south of Fort Bragg to about 70 miles north of Fort Bragg. It was sunny, with a slight haze, and a light wind blowing from west-southwest and brought a marine air mass over the test area.

Five samples were taken during the airborne tests. The first sample, 2160 cc, was taken along the coast about one half to one mile offshore for comparison with forest samples. The elevation during the marine sample collection was 1300 to 2000 feet. This sample probably contains forest emanations from the land breeze cycle, but with aging due to the residence time in the atmosphere. The chromatogram of this sample (1) is shown in Fig. 13.

Samples 2 and 3, 1250 and 2000 cc, respectively, were taken over a forested area at a height of about 200 feet. Gas chromatograms of samples 2 and 3, shown in Fig. 14, are similar, as the conditions of sample collection were quite similar. Peak A is probably acetone, and peak B has the correct elution for α-pinene. Peaks C and D are unknown, but are present in both samples with somewhat different peak height ratios. A slight shoulder (E) on peak D of sample 2 has the appropriate elution time for an unresolved β-pinene peak.

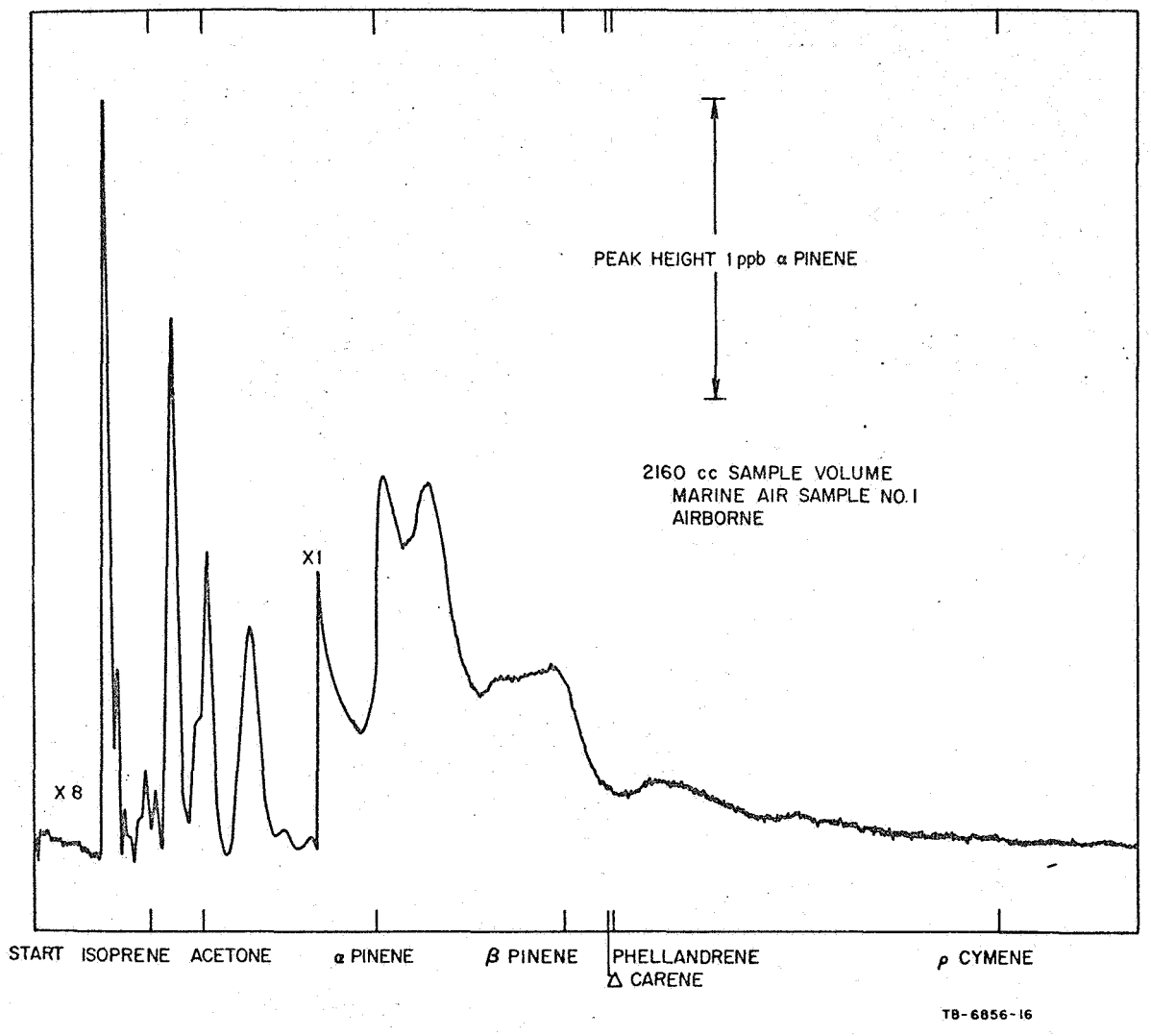

FIG. 13 GAS CHROMATOGRAM SAMPLE NO. 1, AIRBORNE

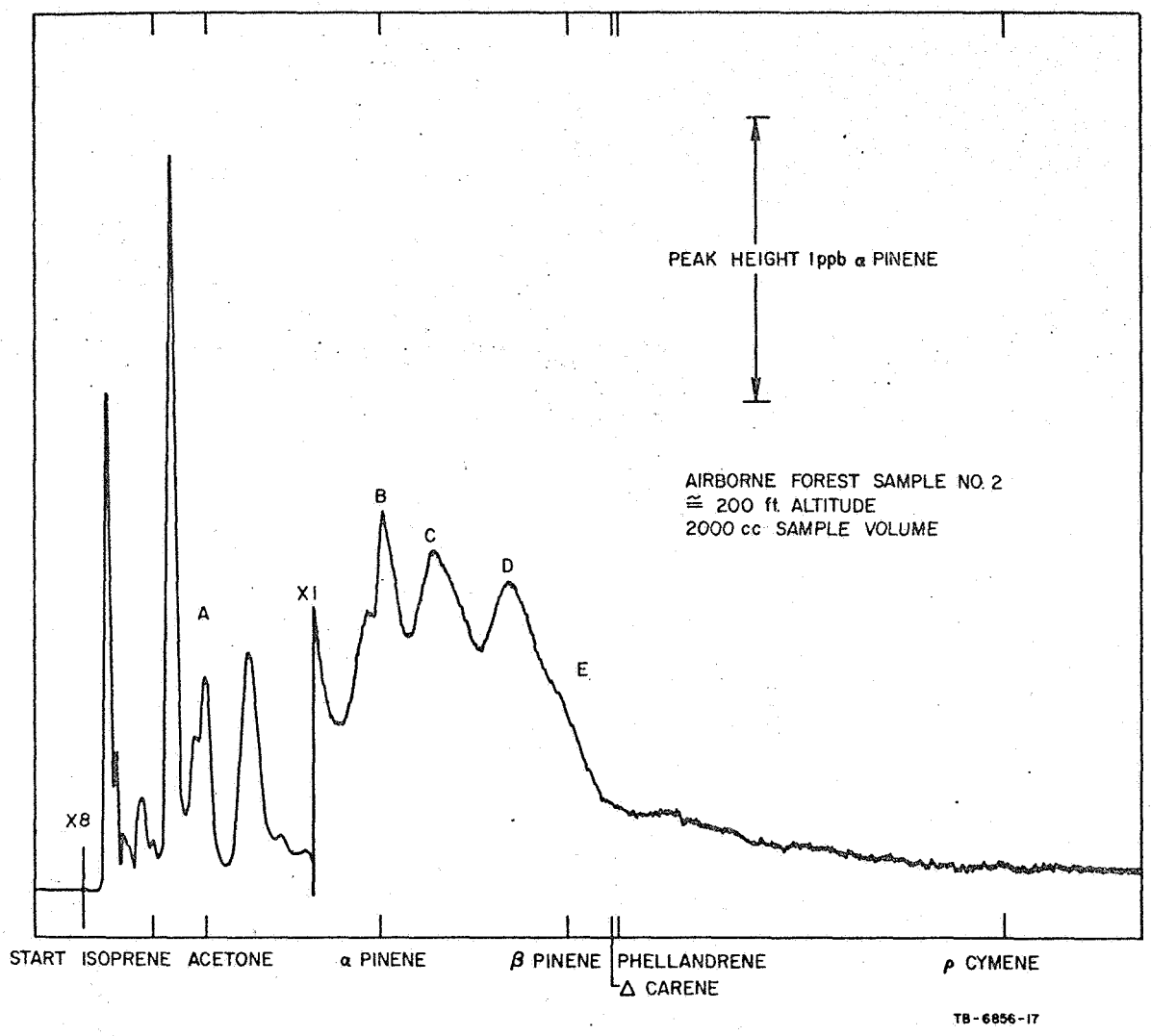

FIG. 14(a) GAS CHROMATOGRAM SAMPLE NO. 2, AIRBORNE

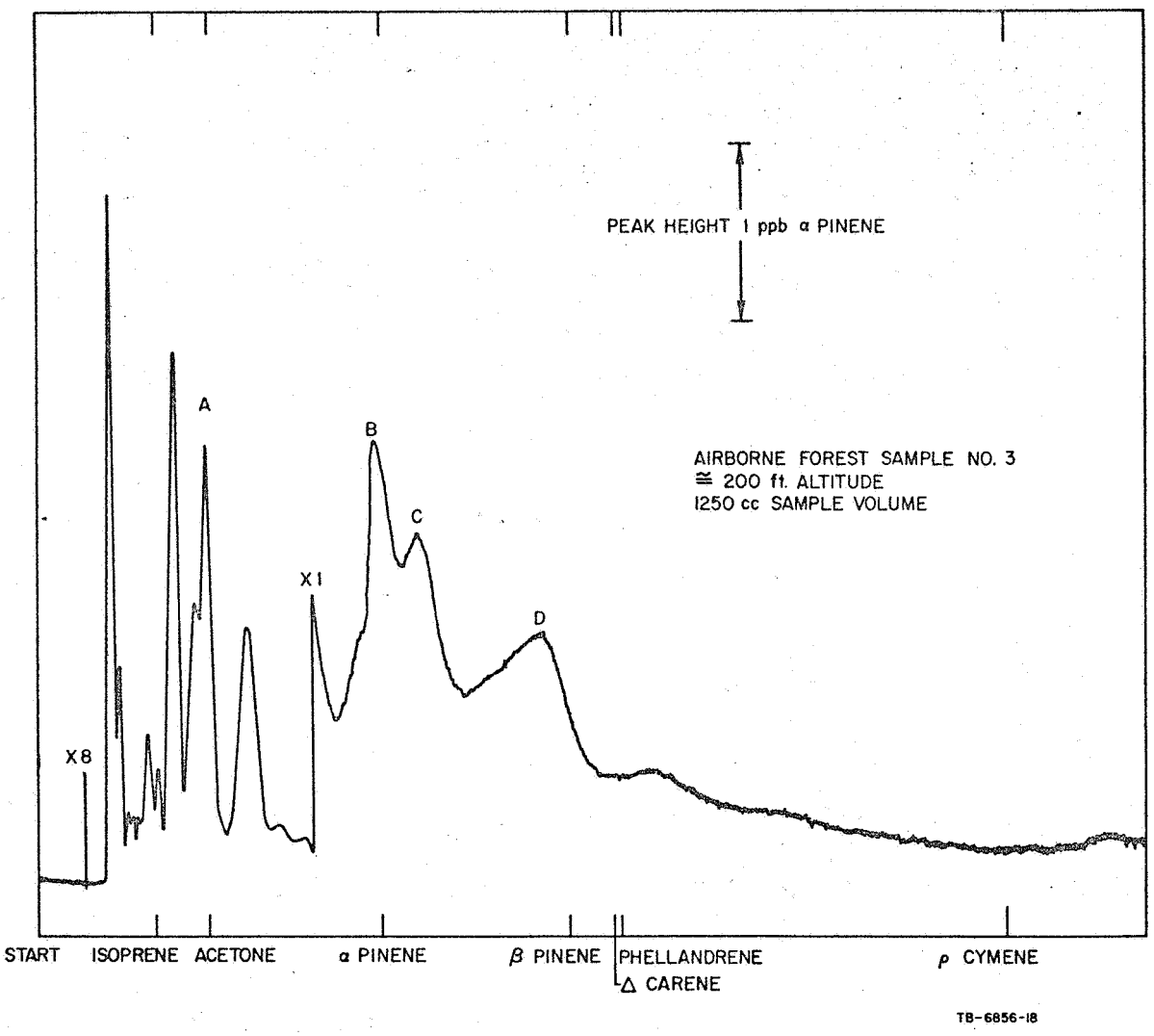

FIG. 14(b) GAS CHROMATOGRAM SAMPLE NO. 3, AIRBORNE

Samples 4 and 5, both 1250 cc, were taken over a forested area at a height of about 800 feet above the trees. Gas chromatograms, shown in Fig. 15, again show reasonable duplication. Sample 5 presents a clearer picture of the late eluting peaks. Peaks B and C are again present, as in samples 2 and 3, with peak B probably α-pinene. Sample 4 has a definite shoulder, E, at the elution time of β-pinene. However, samples from this higher altitude show less resolution in later eluting peaks, indicating the presence of a number of unresolved compounds, or perhaps they are evidence of decomposition products present in airborne organics. The significant changes in the chromatograms of samples taken at two altitudes indicate that additional samples taken at altitude increments up through the troposphere would yield valuable information. Samples taken above 2000 to 3000 feet, where mixing is much less pronounced, might contain different organics as well as lower concentrations. Additional flights with nonpressurized aircraft could yield valuable information, with much less cost, than utilizing jet aircraft for evaluation of the sample collector.

Because of the mountainous terrain, it is impossible to maintain a constant height above the trees. About 10 to 15 miles of terrain were overflown to acquire air samples. The aircraft flight path followed canyons wherever possible, on the assumption that emanations might be more concentrated in sheltered locations. Obviously several canyons must be overflown during a single sample interval.

B. Flight Organic Sample Collector

The design of the flight sample collector suitable for use aboard the NASA Convair 990 has been based on the experience and results of the laboratory and the field sample collection programs. A complete operational diagram of the two-channel flight collector is shown in Fig. 16. Although most of the major components have been purchased and are on hand, the unit has not been assembled.

The operation of the dual-channel unit will be similar in nearly all respects to the detailed operational description given earlier for the single-channel unit and will not be repeated here. The function of

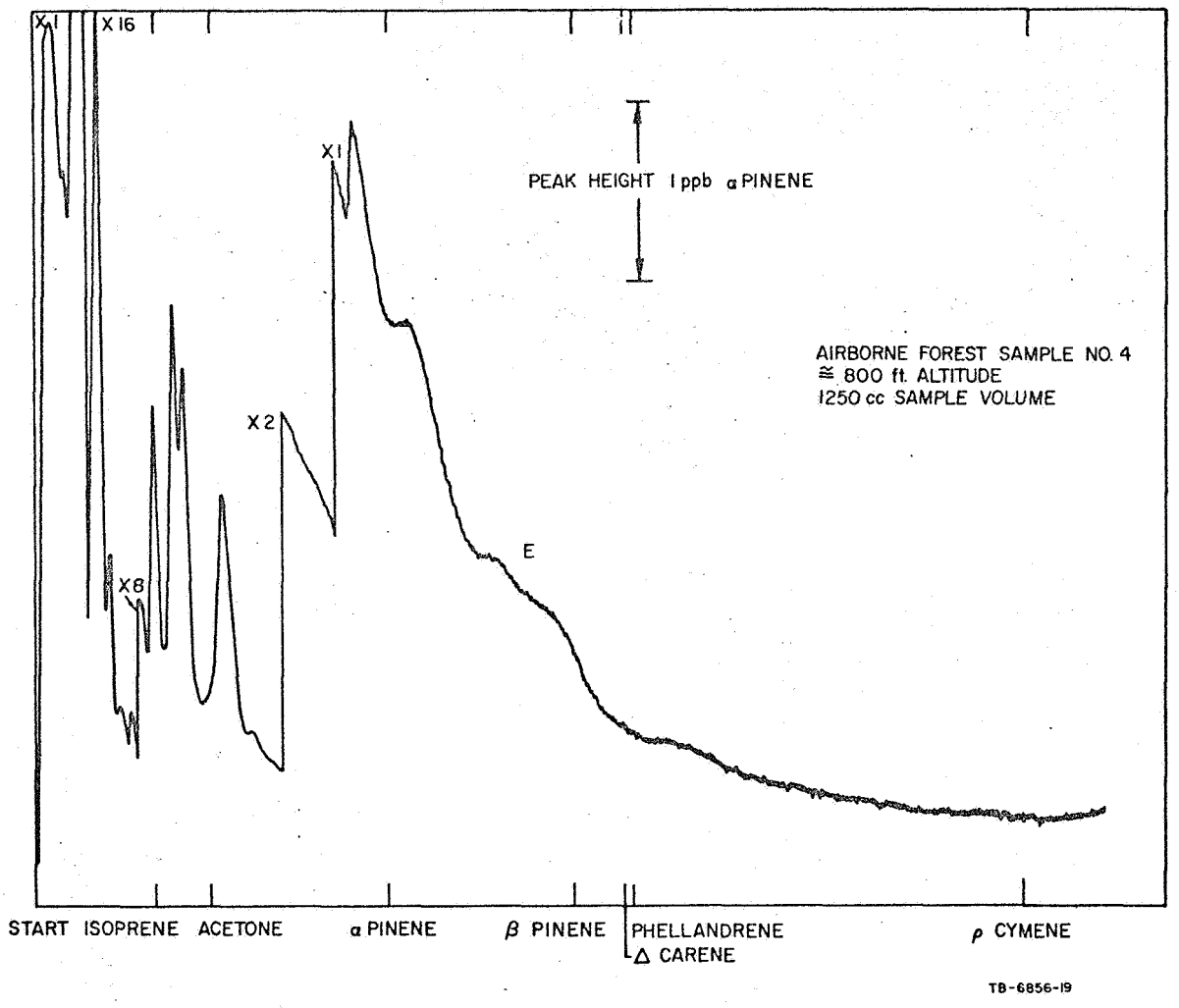

FIG. 15(a) GAS CHROMATOGRAM SAMPLE NO. 4, AIRBORNE

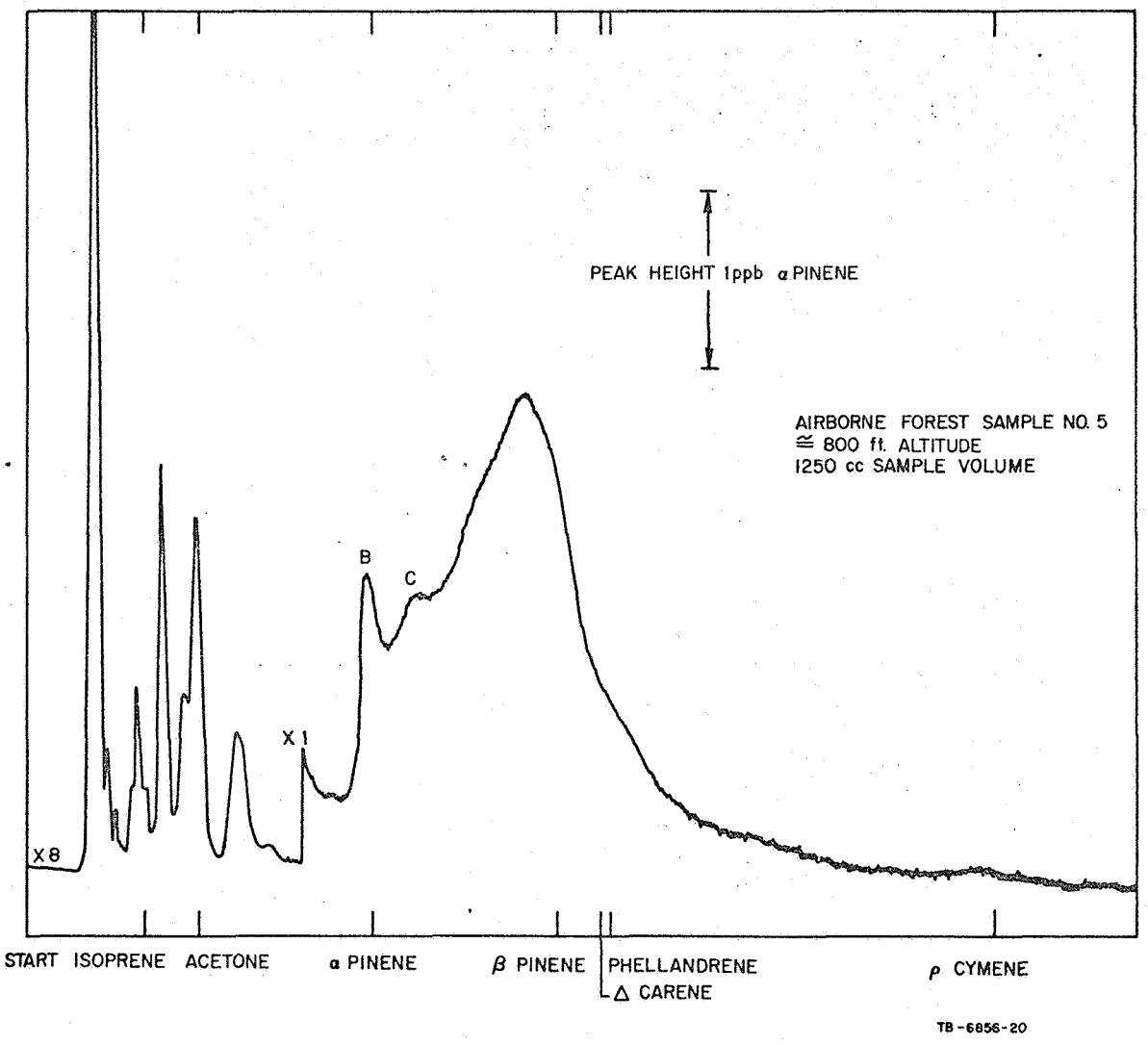

FIG. 15(b) GAS CHROMATOGRAM SAMPLE NO. 5, AIRBORNE

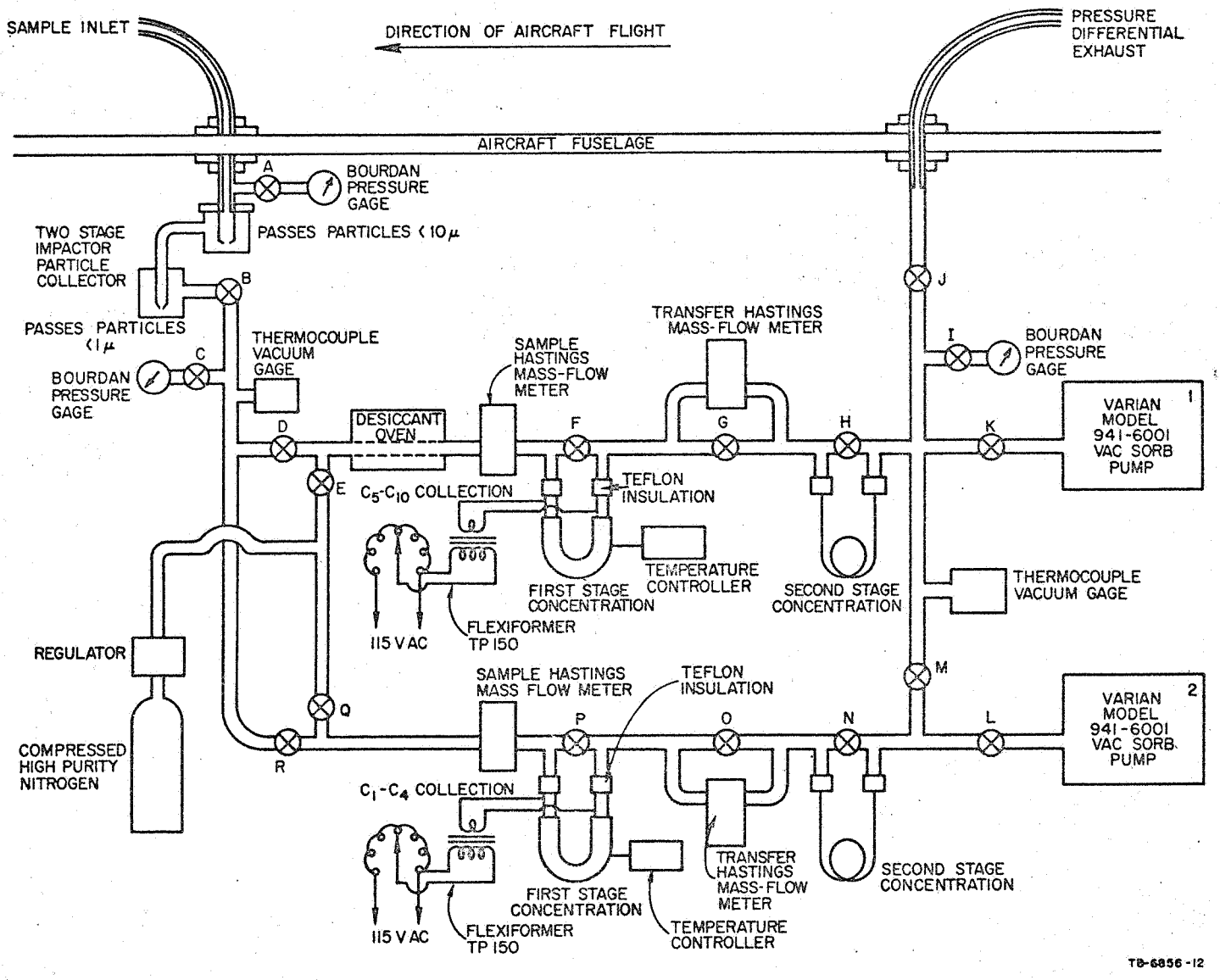

FIG. 16 SCHEMATIC DIAGRAM OF FLIGHT ORGANIC SAMPLER

most controls is obvious from their location in the diagram. The dual-channel unit is designed to have two completely independent sample collection channels. The independent channel design, the dual vacuum pumps, and the pressure differential exhaust vent complicate the valving; therefore a brief description of less obvious component functions will be given.

The sample inlet utilizes the two-stage impactor for the removal of particulate material. The first impactor stage removes particles larger than 10 μ such as ice, snow, and some dust. The second impactor stage removes particles larger than 1 μ. Although an impactor is subject to some changes in performance characteristics with changes in flow rate, performance of this unit should be satisfactory over a broad range of flow rates. The flow rate design center for the two-stage impactor is 1 liter/min. The two Bourdon pressure gauges permit an evaluation of the pressure drop across the impactor stage; thus if clogging, for example, by snow, does occur, the situation becomes immediately obvious. Blockage could be alleviated by blowing the system out with the compressed nitrogen or by disassembly. Valves D, E, Q, and R are necessary to completely isolate each channel during the transfer of sample from the first to second concentration stage. For example, channel 1 can be collecting samples while channel 2 is transferring. The thermal release electrical power is also available independently to each channel. Valves G and O provide a flow bypass of the transfer mass flow meter transducer to obviate the flow restriction of the transducer during sample collection. This will permit higher sample flow rates to be used than were obtainable with the single-channel unit. The pressure differential between the sample inlet and the exhaust port permits sample air flow through the system and should permit sample collection without using the vacuum system at low altitudes. The altitude at which the vacuum pumps must be used during sample collection is a function of the conductance of the system, the velocity of the aircraft, and the sample flow rate required. Valves K, L, and M permit either or both of the vacuum pumps to be utilized for sample collection. This valving arrangement permits either pump to be regenerated in flight in case the volume capacity of a single pump is exceeded through prolonged sampling or by accidentatlly extended

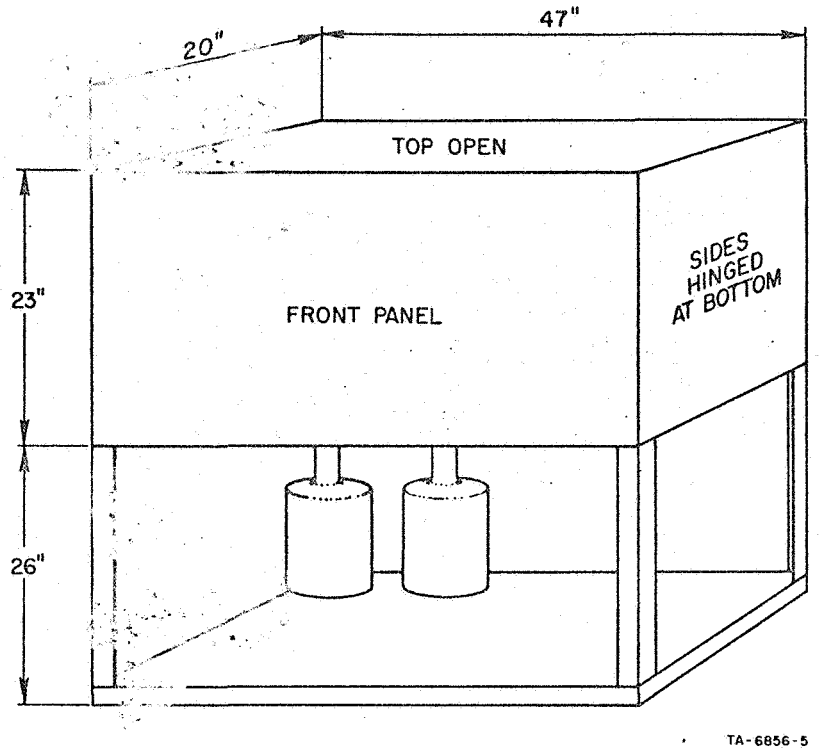

FIG. 17 PHYSICAL CONFIGURATION OF FLIGHT ORGANIC SAMPLER

exposure to the atmosphere. The inlet-exhaust system permits extensive flushing of the [illegible]collector system without exhausting the absorption capacity of the vacuum pumps. Both the inlet and the exhaust ports are sealed with Teflon stoppers until airborne; then nitrogen is used to blow the stoppers free to permit sampling. This pressurization step makes valves A, C, and I mandatory to protect the gauges from damage.

The general configuration and tentative over-all dimensions of the two-channel collection system are shown in Fig. 17. The size of the unit is such that it could be installed in an aircraft much smaller than the Convair 990 specified in the proposal request. It is the understanding of the author that both a Convair 990 and a Lear Jet are available for airborne flight tests of the organic sampler. The prototype two-channel sampler is of such size that installation can be made either in the Convair 990 or a Lear Jet. For low altitude operation a Twin Beechcraft or C-47 could be used. Although it is impossible to provide a finalized layout of the flight instrument until fabrication has been completed, the tentative layout of the front panel is shown in Fig. 18. This panel layout separates the functions of C_5 to C_{10} collection and C_1 to C_4 collection to

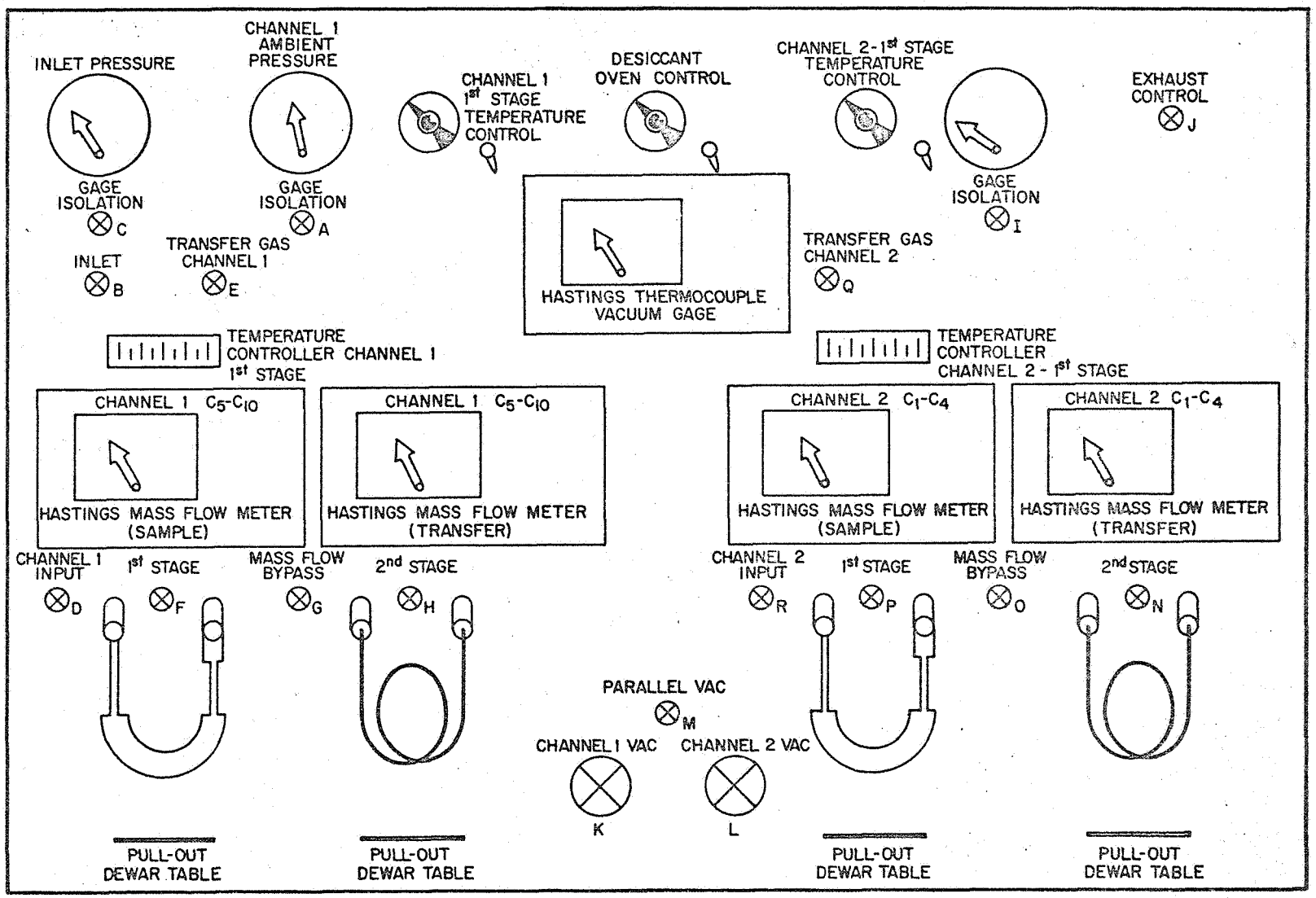

FIG. 18 TENTATIVE FRONT PANEL LAYOUT OF FLIGHT ORGANIC SAMPLER

permit two operators to work at the control panel at the same time if necessary. It is anticipated, however, that a single operator could handle both channels of the sample collection if sampling intervals are slightly staggered.

A list of the major components required for assembly of the two-channel flight airborne organic sample collector is given in the Appendix of this report.

C. External Airborne Sampler Probe

The sampler probe for the flight organic sample collector is of very simple design, shown in Fig. 19. The probe inlet consists of a 1-inch outside, 0.25-inch inside diameter stainless steel tube bent to a 50-cm radius facing forward. A similar tube facing aft will be used as the differential pressure exhaust. The inlet tube will have an inside liner of Teflon tubing that can be removed for clean-up by baking at elevated temperature. Both the inlet and the exhaust are sealed with Teflon plugs to prevent contamination when the aircraft is not airborne. The Teflon plugs are blown free with compressed nitrogen before sampling. Both the inlet and exhaust are sufficiently rugged that they are self-supporting by means of the mounting flange.

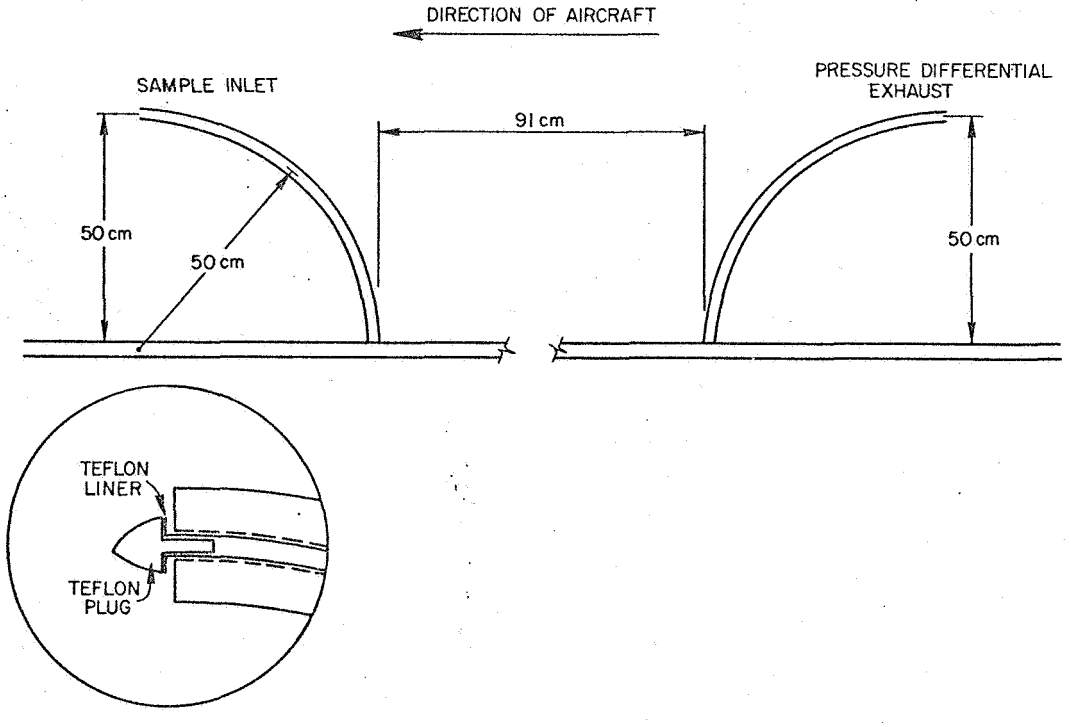

FIG. 19 SAMPLE PROBE FOR FLIGHT ORGANIC SAMPLER

The cross-sectional area requirements of the sample probe design were based on total flow path lengths to the collector unit of 10 to 13 feet at flow rates of 300 to 5000 cc/min. Under worst-case conditions of low velocity at high altitudes (300 mph at 40,000 feet), a cross-sectional area of 2.5 mm^2 would be required; therefore the probe design using an inside diameter of 0.25 inch (27 mm^2) should be adequate. The major consideration of probe area is to eliminate significant pressure drops during operation of the sample collection system.

Another major factor in probe design is the location of the inlet with respect to the aircraft skin. Calculations of the boundary layer thickness for turbulent incompressible flow along a cylindrical fuselage were made at lengths of 9, 15, and 30 meters from the nose of the aircraft by

$$\frac{\delta}{\ell} = 0.37(R_\ell)^{-1/5}$$

where δ = boundary layer thickness

ℓ = length from the nose of the aircraft

R_ℓ = Reynolds number.

The calculations show the boundary thickness to be 12.8, 19.25, and 33.5 cm at 9, 15, and 30 meters from the nose of the aircraft, respectively. Although these calculations are based on incompressible flow, the formula for calculation of compressible flow indicates the actual boundary layer will be thinner. Therefore, the location of the sample inlet at a distance of 50 cm from the fuselage should give more than a 50% safety factor even at a distance of 30 meters from the aircraft nose. The thermal boundary layer thickness was also calculated and should present no problem to sample collection with this probe design. The probe should be located ahead of the leading edge of the wing and ahead of any obstruction that might disrupt the normal flow pattern.

The range of dynamic ram pressures available at the inlet probe during sample collection flights was determined for various altitudes and velocities. Samples can be obtained directly using the pressure differential between the ram pressure at the sample inlet and the low pressure generated

by aspiration at the exhaust port at low altitude. However, at higher altitudes, the vacuum capability of the organic sampler must be used.

The external hardware of the organic sampler inlet probe and exhaust probe is of small cross-sectional area and should cause no significant aerodynamic difficulties. The necessity of performing wind tunnel experiments before flight testing seems very remote.

CONTRIBUTORS

In addition to the author, the following people participated in the experimental work: Mr. Louis J. Salas, Mr. Conrad F. Schadt, and Dr. Cecile Naar. Their contribution to the experimental program is gratefully acknowledged.

APPENDIX

MAJOR COMPONENTS OF THE TWO-CHANNEL ORGANIC SAMPLER

2 Hastings mass flow meters, Model LF5K with transducers*

2 Hastings mass flow meters, Model LF-50 with transducers*

1 Hastings vacuum gauge, Model VT-652*

2 Varian Vac Sorb pumps, Model 941-6001*

2 Type 10 powerstats**

2 Flexiformers, Model TP 150*

2 API temperature controllers, Model 371-K-High*

13 Veeco vacuum valves, Model FL 505 with Teflon seals and seats***

5 Hoke valves, Type 309 A

3 U.S. Model 501S vacuum gauges

2 Varian Model 944-0005 Dewar for Vac Sorb pump*

1 Varian Model heating rod for Vac Sorb pump*

1 desiccant oven (SRI fabrication)*

1 2-stage impactor particle remover

Assorted fittings and tubing

Cabinet frame, front and back panels*

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* Components acquired on present research contract

** 1 Type 10 Powerstat acquired on present research contract

*** 8 Veeco Valves Model FL-505 acquired on present research contract

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